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THE UNIVERSITY OF ALBERTA

NEUTRAL COMPOUNDS OF
HEXACOORDINATE PHOSPHORUS

BY

DIETMAR KARL KENNEPOHL



A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

Spring, 1990



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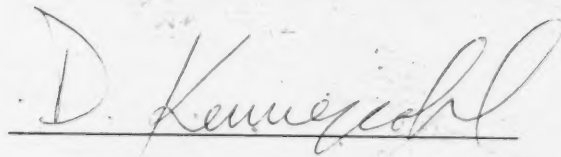
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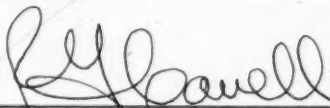
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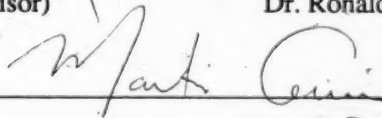
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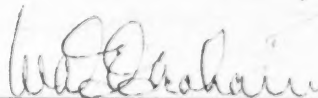


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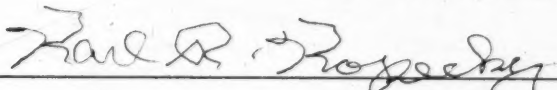
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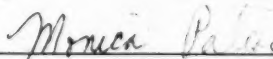
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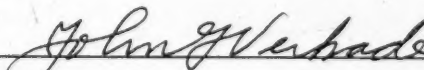
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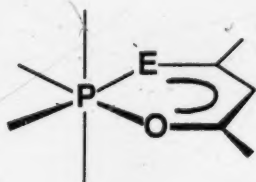
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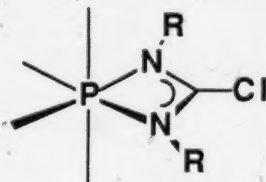
Abstract

Synthetic, structural, and spectroscopic investigations of novel classes of neutral compounds, containing a hexacoordinate (λ^6) phosphorus center, derived from varieties of homo or hetero atomic chelating systems have been undertaken. Representative λ^6 -phosphorus systems are shown below (I-III). Characterization of these compounds, by multinuclear NMR, infrared, and mass spectroscopies coupled with key x-ray crystallographic structures, has shown them to have six-coordinate geometry around phosphorus.



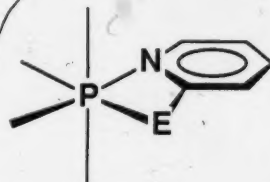
E = O, NH, N(CH₃)

I



R = isopropyl, cyclohexyl

II



E = O, S, N(CH₃), N(Py)

III

The chemical and spectroscopic properties of these compounds are described. These compounds display a characteristic low-frequency (high field) chemical shift (-130 to -205 ppm), in their ³¹P NMR spectra, compared to their pentacoordinate (λ^5) precursors (-35 to -80 ppm). Remarkably, these compounds resist simple substitutions at phosphorus (with such reagents as (CH₃)₄Sn, (CH₃)₃SiSi(CH₃)₃, N(Si(CH₃)₃)₃, and CF₃CH₂OH), but readily hydrolyze to form corresponding phosphoryl (P=O) compounds.

Finally, both the substitutions of the ligands around phosphorus and modifications of the chelating ligand have revealed several trends. For example, in some of these λ^6 -phosphorus compounds, decreasing the basicity of chelating atoms by electron withdrawing groups increases the fluxionality of the compound. In addition to chelating atom basicity, the role of such factors as substituent electron-withdrawing ability and steric hindrance around the central atom in forming λ^6 -phosphorus compounds are discussed.

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ABBREVIATIONS

acac	acetylacetonate
aminoacac	4-aminopent-3-en-2-onate
Bu ⁱ	isobutyl group
DCC	dicyclohexylcarbodiimide
DPC	diisopropylcarbodiimide
Et	ethyl group
H(acac)	acetylacetone
hfa	hexafluoroacetate
H(hfa)	hexafluoroacetone
J	coupling constant (NMR)
K _a	acid dissociation constant
λ	coordination number (e.g. λ^6 = six-coordinate)
M _z	equilibrium magnetization (z component)
Me	methyl group
methylaminoacac	4-methylaminopent-3-en-2-onate
NMR	nuclear magnetic resonance
P	porphyrin
Pc	phthalocyanine
Ph	phenyl group
Pr ⁱ	isopropyl group
Py	pyridine
T ₁	spin-lattice relaxation time (NMR)
trid	tridentate ligand having ONO, ONS, or OOO donor atoms

CHAPTER I

INTRODUCTION

Elements of Groups 13, 14, and 15 display a range of coordination states with the most common being three and four for members of the first row (B, C, N), and four, five or six for the heavier members. In the case of phosphorus the most commonly encountered coordination numbers for neutral compounds are three and four, and a significant but more limited group displaying a five-coordinate environment. Most examples of six coordination are shown by ions of the type PX_6^- (with a variety of X substituents). This work will concentrate on the more rare class of phosphorus compounds displaying six coordination, namely neutral molecules. The preparation and characterization of these neutral high-coordinate molecules is not only a stimulating challenge to the synthetic chemist, but the difficulties explain in part the relatively small number of such examples of high-coordinate phosphorus compounds reported in the literature.

There are several ways of increasing the coordination numbers of a particular main group center element :

- (a) polymerization through bridging ligands,^{1,2}
- (b) formation of simple Lewis acid-base adducts,^{2,3}
- (c) insertion into a macrocyclic ligand,⁴ and
- (d) homo- and heteroatomic chelation by a multidentate ligand.⁵

These and other synthetic routes have led to the discovery of unique compounds containing highly coordinated centers. The increased ability to characterize these novel compounds using modern techniques, such as multinuclear NMR and X-ray crystallography, coupled with development of new synthetic strategies and methods to handle air and thermally sensitive materials, have combined to yield a wealth of new examples of main group

elements in higher coordination numbers. The study of these compounds containing high-coordinate centers has led to:

- (a) identification of their characteristic physical properties,
- (b) an understanding of the chemical nature of coordinatively saturated compounds,
- (c) greater insight into the role of vacant *3d* orbitals in bonding, and
- (d) information regarding various substituent effects that control coordination number.

The work presented in this thesis is specifically concerned with the preparation and characterization of novel neutral compounds containing high coordinate phosphorus. However, some background information about high coordinate main group elements is required at this point to relate our work to previous studies of phosphorus and other neighbouring main group elements. Although this introduction does not give an exhaustive review, important highlights of the chemistry of highly coordinated Group 13, 14, and 15 elements, with emphasis on trends similar to those found in our own phosphorus chemistry, will be described.

1.1 First-Row Elements

Examples of highly coordinated molecules involving first-row elements have generated both interest and controversy.⁶ Five coordinate intermediate species for carbon (eg CH_5^+)⁷ and boron (eg BH_5)⁸ have been proposed. There is still some speculation as to the possible existence of a five coordinate nitrogen species.⁹ These species, which purport to demonstrate the formal expansion of the valence octet for first-row elements,

have not been isolated, because of their transient nature. They have been identified by a variety of specialized techniques, including fission-fragment radiolysis¹⁰, matrix isolation experiments¹¹, low-temperature photolysis¹², kinetic studies¹³, and isotopic exchange studies.¹⁴

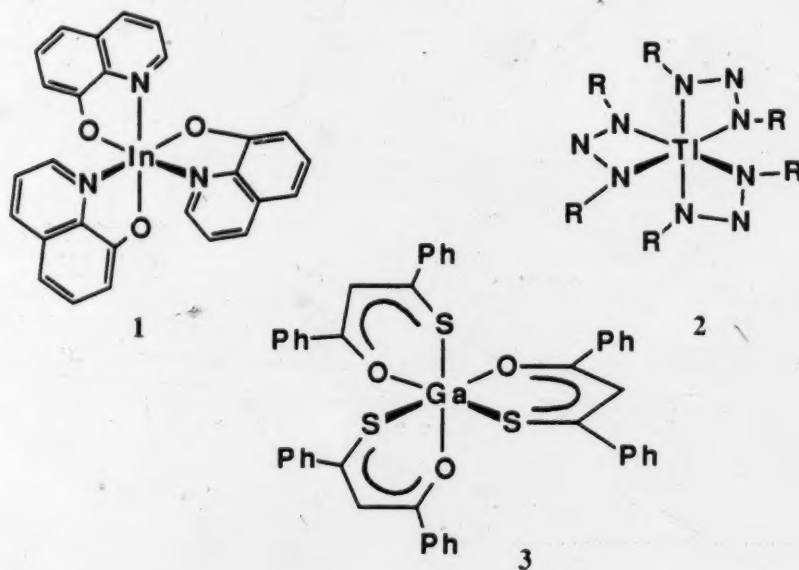
1.2 Group 13 Elements

Simple Lewis acid-base adducts of boron, such as BX_3L_2 , take the ionic form $[BX_2L_2]^+X^-$ (where X = halogen and L = Lewis base),¹⁵ because, unlike the rest of Group 13, boron does not expand its coordination number past four. The metals of Group 13, namely aluminum, gallium, indium, and thallium, form a wide variety of neutral compounds in which the metal is highly coordinated. Several simple adducts have been prepared by coordinating a Lewis base to the Lewis acid center provided by the metal. The range of Group 13 adducts includes amines ($X_3M \cdot nNR_3$),¹⁶ pyridines ($X_3M \cdot nPy$),⁵ dialkylsulfides ($X_3M \cdot nSR_2$),¹⁷ phosphines ($X_3M \cdot nPR_3$),¹⁸ and a large group of compounds containing oxygen donor ligands ($X_3M \cdot nL$, $L = Me_2O, Et_2O, Cl_3PO$)¹⁹ [where $X = H, CH_3$ or halogen and $n = 1$ or 2]. There are, however, some notable exceptions to formation of such adducts by Group 13 elements. Attempts to prepare thallium phosphine adducts failed, because a redox reaction takes place. The thallium is easily reduced from $Tl(III)$ to $Tl(I)$ while the phosphine is oxidized from $P(III)$ to $P(V)$.²⁰

The most common group of neutral compounds containing highly coordinated Group 13 elements are formed from bidentate chelates, such as acetylacetone ($Hacac$). Three such chelates can be attached to the metal to form a neutral compound with a six-coordinate center. The acetylacetonates, $Al(acac)_3$,²¹ $Ga(acac)_3$,²² and $In(acac)_3$ ²³ have long been established. However, to date the corresponding $Tl(acac)_3$ has not been prepared. There are many other examples of bidentate ligands containing oxygen donors, such as tropolone,²⁴ which can form similar compounds with Group 13 elements. These

chelates are generally formed by means of substitution reactions of MX_3 (where $\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{or Tl}$ and $\text{X} = \text{halogen}$). Each halogen is replaced by a bidentate ligand resulting in a neutral compound with a hexacoordinate MO_6 kernel. Another common group of ligands which form hexacoordinate Group 13 metal complexes is the carboxylates. Well known examples of carboxylates include $\text{Al}(\text{O}_2\text{CR})_3$,²⁵ $\text{Ga}(\text{O}_2\text{CR})_3$,²⁶ $\text{In}(\text{O}_2\text{CR})_3$,²⁷ and $\text{Tl}(\text{O}_2\text{CR})_3$ ²⁸ (where $\text{R} = \text{CH}_3$ or CF_3).

The MS_6 kernel (where $\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{or Tl}$) is also well established with such bidentate sulfur ligands as dithiocarbamate, dithiobenzoate, dithiophenylacetate, diphenyldithioarsenate, and the xanthates. Generally, these neutral compounds are also prepared by a simple substitution reaction of MCl_3 replacing Cl with the bidentate disulphide ligand. However, the dithiocarbamates can also be prepared from an apparent CS_2 insertion into the M-N bond of $\text{M}(\text{NMe}_2)_3$ to form $\text{M}(\text{S}_2\text{CNMe}_2)_3$.²⁹ Many other chelating ligands containing N, S and O linking atoms have been used to form Group 13 compounds with five and six coordination. Examples of such Group 13 compounds include structures 1-3 shown below:^{30,31,32}



Another important class of Group 13 compounds with high coordinate centers involve macrocyclic ligands. The two most common macrocycles which have been used are the phthalocyanines (Pc) and the porphyrins (P). These ligands are large planar organic molecules with a central cavity large enough to accommodate a metal ion. The metal atom in this cavity is held in place by four nitrogen binding sites defining a N_4 plane.

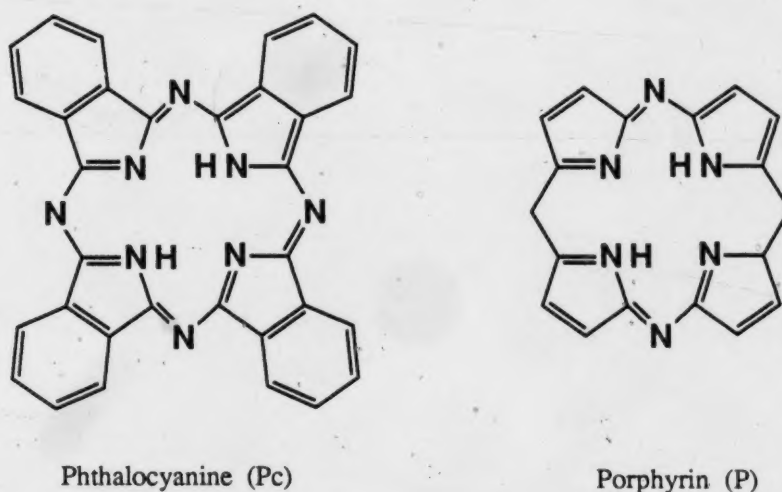
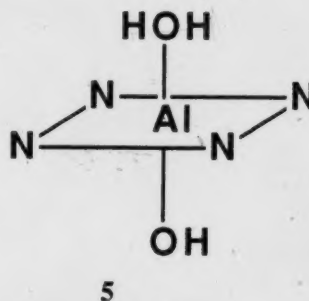
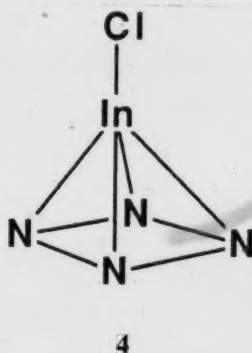


Figure 1.1 Structures of phthalocyanine and porphyrin.

These neutral phthalocyanine and porphyrin derivatives with high-coordinate centers display unusual properties, which draw a wide variety of research interests. The phthalocyanines of Al, Ga and In are being studied as photocatalysts,³³ and polymeric fluoro-gallium (or fluoro-aluminum) phthalocyanines (e.g. $[PcGaF]_n$) display high electrical conductivity.³⁴ Some metalloporphyrins, such as tetraphenylindium(III)chloride, with five-coordinate indium in a neutral molecule, are being investigated as model compounds for myoglobin or hemoglobin.^{4,35}

These macrocyclic compounds can provide the basis of a five-coordinate environment usually in the form of a square-based pyramidal geometry in which the metal

sits just above the N_4 plane of the macrocycle. They are prepared from the reaction of the phthalocyanine (Pc) with the metal chloride (MCl_3), eliminating two moles of HCl to give $(Pc)MCl$ with five coordination. They can also form an octahedral arrangement around the metal in further reaction with an additional ligand, for example, hydrolysis of $(Pc)MCl$ gives $(Pc)M(OH)(H_2O)$ with a six-coordinate center. Subsequent reactions of $(Pc)M(OH)(H_2O)$ yield other neutral Group 13 compounds with a six-coordinate center. Examples of both the five- and six-coordinate geometries are illustrated by structures 4 and 5, below:^{4,36}



1.3 Group 14 Elements

Group 14 elements, which commonly exhibit four coordination, are known to occasionally form compounds with higher coordination of the element. With the exception of some caged metal cluster compounds,³⁷ no neutral molecules of five-coordinate carbon are known. The lighter Group 14 elements, namely silicon and germanium, can display five and six coordination in a neutral compound. The remaining metallic members of Group 14 (tin and lead) can even expand their coordination number to seven or eight.

The heavier Group 14 members Sn(IV) and Pb(IV) are generally found in four-coordinate environments similar to other elements of Group 14. However, these metals can also display a variety of higher coordination numbers. In some cases, the state of the compound plays an important role in determining the coordination number. For example, SnF_4 is tetrahedral in solution and in the gas phase, but in the solid state it forms a two dimensional fluorine-bridged sheet structure in which the tin is six coordinate.³⁸ Similarly, PbCl_2Ph_2 is also tetrahedral in solution and in the gas phase, but forms linear chains in the solid state in which lead achieves six coordination by accepting electron pairs from bridging chlorines.³⁹

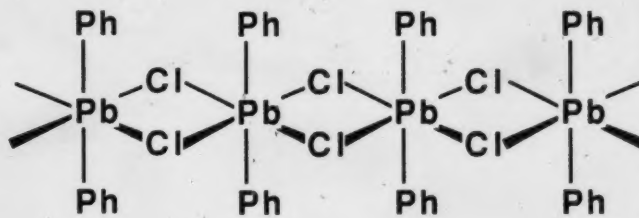
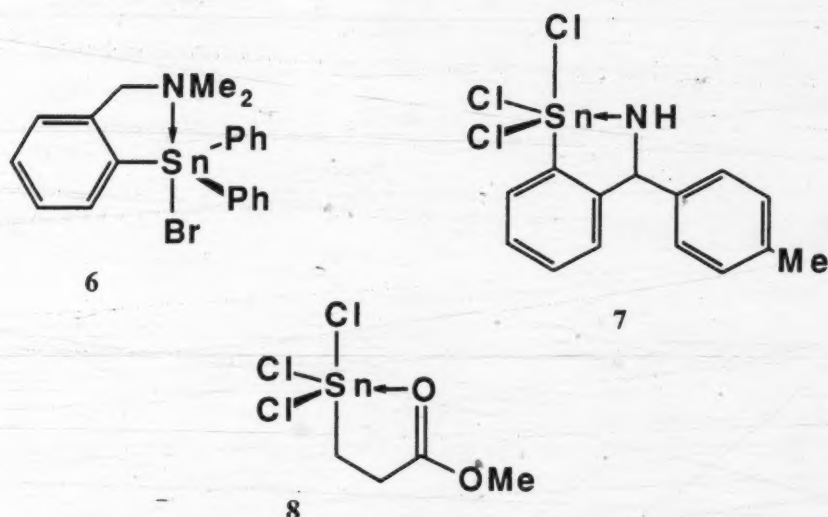


Figure 1.2 Linear chain of PbPh_2Cl_2 .

The first authentic complex containing a five coordinate tin atom, $\text{Me}_3\text{SnCl}:\text{Pyridine}$, was prepared by Huhne in 1962.² Many such simple Lewis acid-base adducts are known with presumably similar structures. Several other neutral tin compounds containing a five-coordinate center have since been characterized. Essentially, these more complex examples are formed by an organic ligand attached to the metal that contains a free Lewis base function at the other end (O or N) which can bend around and bind to the metal (illustrated by structures 6-8).^{40,41,42}

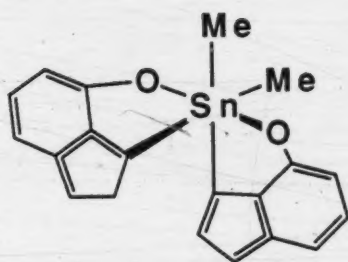


Bidentate chelating ligands have also been used to form compounds containing five-coordinate tin and lead. The λ^5 -triorganotin and lead acetylacetonates (9) and N-acylhydroxylaminates (10) are among the more established examples.^{43,44,45}

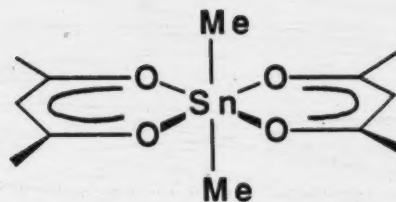


Curiously, tin and lead compounds which contain three metal-carbon bonds appear to have a coordination saturation of five. The only authenticated exception to this trend is the pyrazolylborate tin complex, $\text{Me}_3\text{Sn}[(\text{N}_2\text{C}_3\text{H}_3)_3\text{BH}]$,⁴⁶ which is an example of a neutral triorgano compound containing hexacoordinate tin.

In contrast, there are numerous neutral diorgano tin and lead compounds with hexacoordinate geometries. The bisoxinates (11) and bisketonates (12) are among the most common examples.^{47,48}



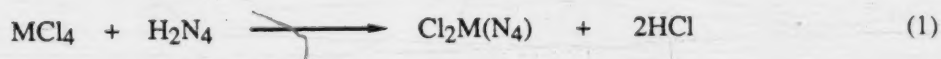
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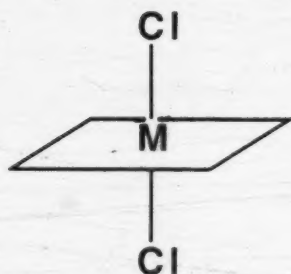
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Neutral bisdithiocarbamates, such as $\text{Me}_2\text{Sn}[\text{S}_2\text{CNMe}_2]_2$, in which both the dithiocarbamates act as a bidentate ligands, provide a six-coordinate tin center. In the corresponding triorgano compounds the two dithiocarbamates act as unidentate ligands leading to only five-coordinate tin centers.⁴⁹ Other sulfur chelate derivatives, such as dithiophosphinates of lead and tin ($\text{Ph}_2\text{Pb}[\text{S}_2\text{P}(\text{OPr}^i)_2]_2$ ⁵⁰ and $\text{Ph}_2\text{Sn}[\text{S}_2\text{P}(\text{OEt})_2]_2$ ⁵¹), provide well-documented examples of hexacoordinate elements. The biscarboxylates of diorgano tin and lead compounds also form neutral compounds with hexacoordinate centers, generally with bridged structures in the solid state and chelates in solution.⁴⁴

Similar to the Group 13 elements, several compounds of Group 14 elements form high-coordinate centers with organic macromolecules. The two largest and best known classes are, as before, the phthalocyanines^{36,52} and the porphyrins.^{52,53} All these compounds are readily prepared from the exothermic reactions (eq. (1)) of the metal chloride (SnCl_4 or PbCl_4) and the free ligand (H_2N_4), forming an octahedral arrangement around the central metal.



In these products, the two chlorine atoms lie above and below the plane of the macrocycle containing the metal atom, as illustrated in 13.

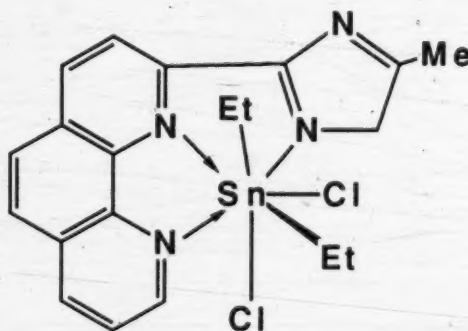


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These remaining chlorine atoms can easily be replaced by other ligands. For example, the dihydroxy analogue can be prepared by treatment of the dichloride with an ethanol-ammonium hydroxide mixture (eq. (2)).



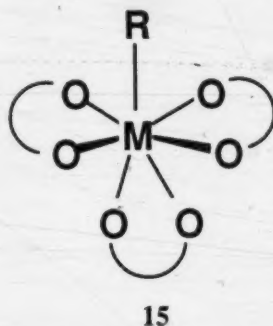
In addition to several examples of tin and lead compounds, with a six-coordinate center, there are a few examples displaying heptacoordination. Similar to the coordination saturation of five shown by triorgano tin and lead, the diorgano tin and lead compounds have an apparent coordination of six. One rare exception to this coordination saturation is a tin compound coordinated by a tridentate ligand to form the λ^7 tin compound **14**.⁵⁴



14

In contrast, the neutral monoorgano tin and lead derivatives regularly display heptacoordination with bidentate ligands such as the triscarboxylates⁵⁵ and the

trinitrates.⁵⁶ In these cases, the organosubstituted (R) metal is chelated by three of these bidentate ligands to form a neutral λ^7 -metal compound (15).

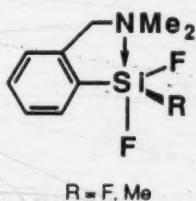


Finally, octacoordination of tin and lead is possible in neutral compounds if four bidentate ligands are bound to the metal. The tetraacetates, $M(O_2CMe)_4$, of tin⁵⁷ and lead⁵⁸ have been reported. Octacoordination has not been reported for the lighter elements of Group 14. For example the analogous tetraacetate of silicon, $Si[OC(O)Me]_4$, is a tetrahedral λ^4 compound in which the acetates behave as unidentate ligands.⁵⁹ The corresponding acetate anions of Si and Ge, $[M(OC(O)Me)_6]^{2-}$, are reported to be hexacoordinate with unidentate ligands.⁶⁰

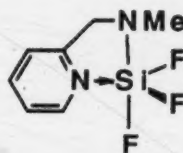
Comparisons of the nature of silicon and germanium against the first-row element, carbon, are of special interest. Carbon does not serve as a model for prediction of the chemistry of the Group 14 elements. Unlike carbon, silicon can accommodate up to twelve electrons in its valence shell. This difference between carbon and silicon is reflected in their reactivities. For example, CCl_4 reacts poorly with water, but $SiCl_4$ will hydrolyze immediately and completely on contact.

Compounds containing six-coordinate silicon were known in the early 19th century. Gay-Lussac discovered $F_4Si \cdot 2NH_3$ ⁶¹ in 1809 and three years later Davy obtained the same compound.⁶² Other six-coordinate silicon compounds followed, including fluorosilicic acid, H_2SiF_6 , and its salts, the hexafluorosilicates.⁶³ In subsequent

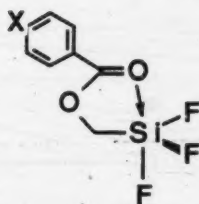
decades a few adducts of silicon tetrahalides with tertiary amines (similar to Gay-Lussac's $\text{F}_4\text{Si} \cdot 2\text{NH}_3$) were synthesized. In the first part of the 20th century silicon diketonates were investigated⁶⁴ and the presence of $\text{Si}(\text{OH})_6^{2-}$ ions in silica was proposed.⁶⁵ In the second half of this century several new classes of five- and six-coordinate silicon compounds were discovered.⁶⁶ Progress in the identification of such species was prompted by the availability of new experimental techniques, both in new synthetic approaches and in the use of multinuclear NMR and X-ray crystallography for characterization. In addition, specific biological activity was observed for some of the silicon compounds with expanded coordination sphere, which provided an impetus for further study.⁶⁷ Some recent examples of neutral compounds with pentacoordinate Si and Ge include structures 16-20.^{68,69,70,71,72}



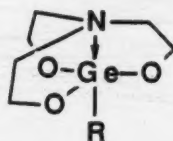
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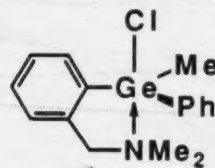
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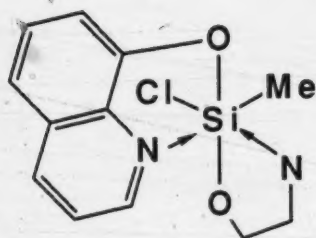


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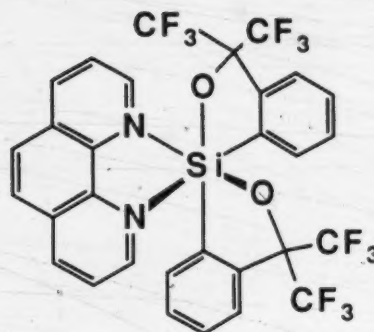


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Neutral compounds containing hexacoordinate silicon and germanium are not as common as those showing five coordination. As with Sn and Pb, high-coordination of Si and Ge can be achieved through the binding of organic bidentate chelating ligands to the central "metal-like" atom, as illustrated by structures 21 and 22.^{73,74}



21



22

Also, similar to the behaviour of Sn and Pb, six-coordinate Si and Ge can be prepared with porphyrins and phthalocyanines. Preparation of the phthalocyanines of silicon and germanium require much higher reaction temperatures as compared to tin and lead. Typically, SiCl_4 or GeCl_4 reacts in a phthalonitrile-quinoline solution at 200°C .⁵² Preparations of the porphyrins of germanium and silicon also require more drastic reaction conditions than those of tin and lead. For example, heating SiCl_4 (or GeCl_4) and the free porphyrin to 170°C in a sealed tube for several hours gave only low yields of the neutral silicon or germanium compound with a six-coordinate center.⁷⁵

Factors such as ligand electronegativity, steric interaction, and ring size formed by the chelating ligand are important parameters controlling the formation of compounds of five- and six-coordinate silicon. Both the five- and six-coordinate silicon is favoured when:

- (a) bulk steric interactions between substituents are minimized;
- (b) chelating ligands form five membered rings (which are less sterically demanding than six or seven membered rings); and
- (c) the electronegativity of the substituents is increased.

Similar considerations are important for the formation of compounds containing hexacoordinate phosphorus, as will be discussed later in more detail.

Both silicon and its neighbour phosphorus share another important characteristic when these highly coordinated centers develop; the NMR chemical shift of ^{29}Si and ^{31}P nuclei show a definite lowering of the resonance frequency (upfield shift) as their coordination number is increased. This trend has also been established for other main group elements, such as ^{119}Sn , and has been markedly demonstrated through the series as coordination number increases from λ^5 to λ^6 to λ^7 -Sn.⁷⁶ This suggests that the central atom (^{29}Si , ^{119}Sn , or ^{31}P) is being increasingly shielded by the electrons donated by the extra ligands provided in the more highly coordinated environments. This trend has been established reliably enough to serve for the diagnosis of the formation of the more highly coordinated center.

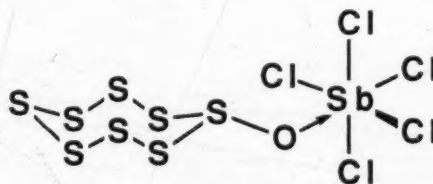
1.4 Arsenic, Antimony, and Bismuth

The list of neutral compounds of arsenic, antimony, and bismuth containing a six-coordinate center is meagre. Examples can generally be subdivided into three categories:

- (a) simple Lewis acid-base adducts,
- (b) neutral compounds containing the six-coordinate element in an M(III) oxidation state, and
- (c) neutral compounds containing the six-coordinate element in an M(V) oxidation state.

Group 15 elements can form simple adducts with Lewis bases. The six-coordinate antimony adduct, $\text{SbCl}_5 \cdot \text{SeOCl}_2$, has been known since the middle of the last century,⁷⁷

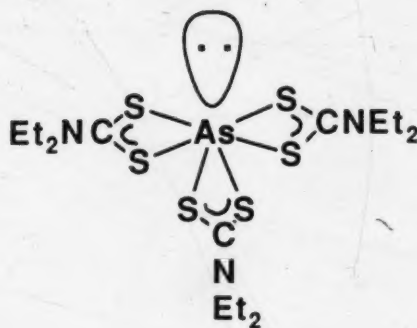
but has only recently been fully characterized by an x-ray diffraction study.⁷⁸ Another unusual antimony adduct is $\text{S}_8\text{O}\cdot\text{SbCl}_5$ (**23**), in which the monooxidized S_8 ring remains intact.⁷⁹



23

Adducts containing hexacoordinate arsenic can also form, for example $\text{AsF}_5\cdot\text{N}(\text{Me})\text{SOF}_2$.⁸⁰ Finally, a few addition compounds of six-coordinate bismuth such as $\text{BiCl}_3(\text{NH}_3)_3$, $\text{BiCl}_3(\text{NO}_2)_3$, and $\text{BiCl}_3(\text{SC}_5\text{H}_4\text{N})_3$ have been recently reported.⁸¹

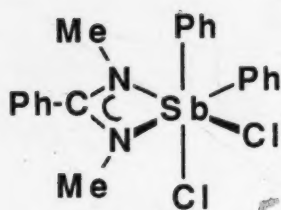
A large number of neutral compounds of these Group 15 elements surprisingly involve high coordination of the lower $\text{M}(\text{III})$ oxidation state. For example, $\text{As}(\text{S}_2\text{CNEt}_2)_3$ (**24**) prepared fifty years ago by Malatesta,⁸² was recently structurally characterized⁸³ and shown to contain a hexacoordinate arsenic atom. Around the arsenic there are three short As-S bonds (2.3 Å) and three longer As-S bonds (2.9 Å) trans to the short bonds. In addition, the structure indicates that space is provided for a lone pair of electrons, making the geometry around arsenic pseudo-seven coordinate.



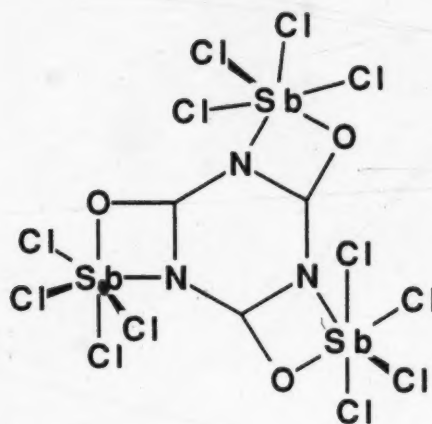
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Several such examples of six-coordinate As(III), Sb(III), and Bi(III) with seven pairs of electrons around the central atom exist. The arsenic selenocarbamate series $\text{As}(\text{Se}_2\text{CNR}_2)_3$ (where $\text{R} = \text{Et}$, Bu^i , or CH_2Ph)⁸⁴ and the antimony dithio series SbL_3 (where $\text{L} = \text{S}_2\text{CNEt}_2$, $\text{S}_2\text{C}(\text{NC}_5\text{H}_{10})$, S_2PPh_2 , $\text{S}_2\text{P}(\text{OMe})_2$, S_2COEt)⁸⁵ are examples involving homoatomic bidentate ligands. The corresponding Bi(III) carbamates and thiocarbamates, $\text{Bi}(\text{X}_2\text{CNR}_2)_3$ (where $\text{X} = \text{O}$ or S and $\text{R} = \text{alkyl group}$), also exist and are prepared by an apparent insertion of CX_2 into the Bi-N bond of $\text{Bi}(\text{NR}_2)_3$. These M(III) neutral hexacoordinate compounds can also be generated using heteroatomic bidentate ligands, such as thioloibenzoate or 8-hydroxyquinone.⁸⁶ Again, in a similar reaction to that used to form the carbamates, $\text{Bi}(\text{NR}_2)_3$ undergoes an apparent insertion with phenylthiocyanate ($\text{PhN}=\text{C}=\text{S}$) to form $\text{Bi}[\text{SC}(\text{NPh})\text{NR}_2]_3$ with hexacoordinate bismuth.

Compounds containing hexacoordinate Group 15 element centers in the M(V) oxidation state are also known. The most abundant are antimony compounds that contain a bidentate ligand, such as in the series $\text{R}_3\text{Sb}(\text{OMe})\text{L}$ (where $\text{R} = \text{alkyl}$ and $\text{L} = \text{acetylacetone}$, 8-hydroxyquinone, salicylaldehyde, o-hydroxyacetophenone, 2-hydroxynaphthaldehyde).⁸⁷ Two hexacoordinate Sb(V) compounds worth noting are the dimethylbenzamidine (dmb) derivative $\text{Ph}_2\text{Sb}(\text{dmb})\text{Cl}_2$ (**25**),⁸⁸ which is analogous to several six-coordinate P(V) compounds to be discussed later, and the structurally curious tetrachloroisocyanate $[\text{SbCl}_4\text{NCO}]_3$ (**26**).⁸⁹

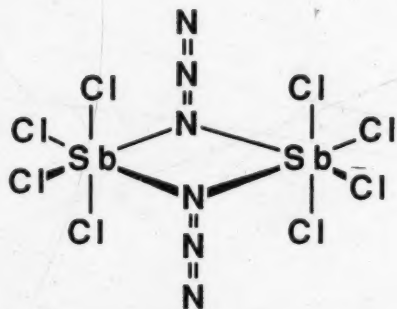


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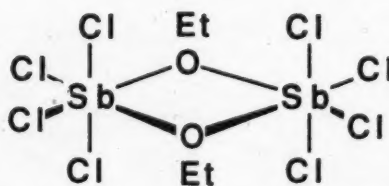


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The latter unusual isocyanate structure (**26**) was prepared from $\text{K}[\text{SbCl}_5\text{NCO}]$ and SbCl_5 in liquid SO_2 . Initially a bridged compound $[\text{SbCl}_4\text{NCO}]_2$ is formed, which contains a high coordinate antimony center. This bridged isocyanate is thermally stable only to -20°C , and at higher temperatures it eventually forms the more stable trimer $[\text{SbCl}_4\text{NCO}]_3$. Other bridged Sb(V) compounds similar to $[\text{SbCl}_4\text{NCO}]_2$, such as $[\text{SbCl}_4\text{N}_3]_2$ (**27**)⁸⁹ and $[\text{SbCl}_4\text{OEt}]_2$ (**28**)⁹⁰ have also been reported.



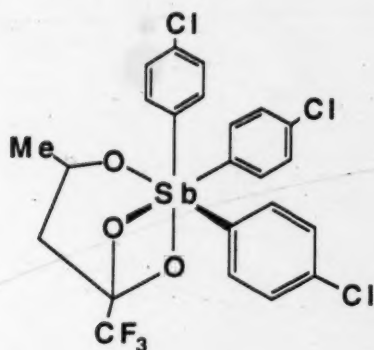
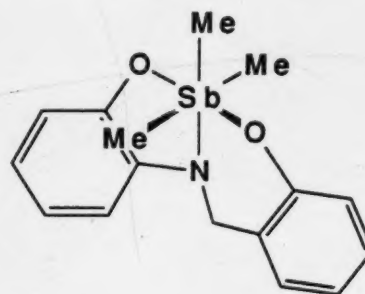
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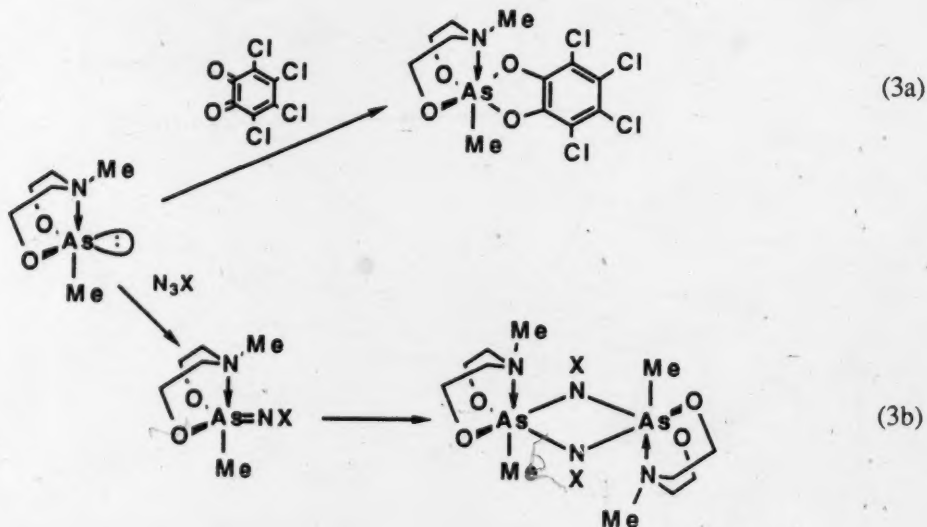
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The use of tridentate ligands to form compounds of six-coordinate Sb(V) has also been recently reported. The compounds are generally of the type $\text{SbR}_3(\text{trid})$ or $\text{SbClMe}_2(\text{trid})$

(where R = alkyl or aryl and trid = tridentate ligand having ONO, ONS or OOO donor atoms). Examples include **29** and **30** shown below:^{91,92}

**29****30**

Finally, only two examples of neutral compounds containing six-coordinate As(V) have been reported and both involve a tridentate ligand having ONO donor atoms. They are formed from the four-coordinate arsatrane, $\text{MeAs}[(\text{OC}_2\text{H}_4)_2\text{NMe}]$ (shown below) by either a Kukhtin-Ramirez reaction (eq. (3a))⁹³ or a Staudinger reaction followed by dimerization to form the bridged species (eq (3b)).⁹⁴



1.5 Phosphorus

1.5.1 Electronic Arrangement

The electronic arrangement of pentavalent phosphorus has been the subject of much debate over the years. This is in contrast to the situation which prevails for tricoordinate P(III) compounds, in which three phosphorus electrons are considered to form σ bonds with three other atoms, leaving the remaining two electrons as a nonbonding lone pair. The valence structure thus involves eight electrons and parallels the models developed for first-row elements with an octet structure. The principal controversy in the electronic structure of P(V) compounds is the possible participation of $3d$ orbitals in bonding. The detailed arguments both for and against $3d$ -orbital involvement have been thoroughly discussed and reviewed elsewhere.^{95,96} Some believe that spd hybridized orbitals, such as sp^3d and sp^3d^2 , are required to generate five- and six-coordinate phosphorus centers, respectively. However, others believe that the σ framework for four-, five-, and six-coordinate phosphorus can be formulated exclusively from s and p or sp hybridized orbitals because the amount of energy required to promote a phosphorus $3s$ or $3p$ electron to the $3d$ level is too large to allow any d -orbital involvement. In addition, Slater-type equations for $3d$ -orbital distribution functions show that these d orbitals are much too diffuse to overlap with bonding orbitals of approaching ligands. The counterargument, in favour of d orbitals, points out that these Slater-type calculations are based on hydrogen-like orbitals which have a different radial density distribution compared to phosphorus. Also, the association of phosphorus with strong electron withdrawing ligands, such as fluorine, chlorine, and oxygen, serves to contract the d orbitals and lower their energy. However, in spite of this orbital-contraction hypothesis, d -orbital opponents note that the $4s$ and $4p$ orbitals would also be reduced in energy to an extent that would ensure their participation. It would seem that for every argument for d -orbital involvement there is a counterargument. In addition,

data obtained from physical techniques⁹⁷ (such as nuclear quadrupole coupling, ESR, and UV experiments) to confirm *d*-orbital contributions in bonding is inconclusive.

There is some strong evidence that does suggest *d*-orbital involvement in the π interactions in second-row elements which should be noted. Observations such as:

- (a) the S-O bonds in sulfoxides and sulfones are less polar than expected,⁹⁸
- (b) the bond angles of Si-O-Si or Si-N-Si are wider than expected,⁹⁵
- (c) the arrangement of P-NH₂ in F₂P-NH₂ is planar,⁹⁹ and
- (d) the P-O bond in phosphoryl compounds such as F₃PO is surprisingly strong,¹⁰⁰

have all been attributed to $d\pi-p\pi$ interaction. For example, in F₃PO the phosphorus forms an sp^3 framework one component of which forms a σ -bond with oxygen. Then the lone pair of electrons on oxygen is thought to "back-donate" to an empty 3*d* orbital of phosphorus to form a $d\pi-p\pi$ bond (Figure 1.3) using a symmetrically correct coplanar *d* orbital on phosphorus.

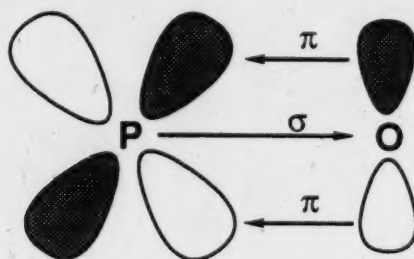


Figure 1.3 Back donation to form $d\pi-p\pi$ bond.

Another example which provides evidence for π -bonding in phosphorus compounds is the behaviour of pentacoordinate F₄PSR.¹⁰¹ Restricted rotation of the SR group (as shown

by NMR) suggests back-donation of electron density from the filled p orbitals of the sulfur to an empty $3d$ phosphorus orbital (Figure 1.4).

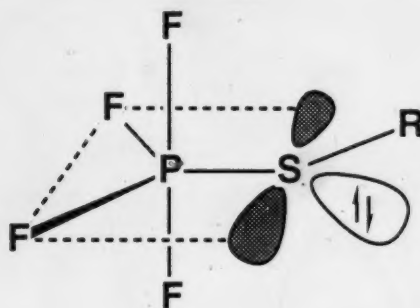


Figure 1.4 Geometry of F_4PSR adapted from Emsely and Hall *The Chemistry of Phosphorus*.⁹⁶

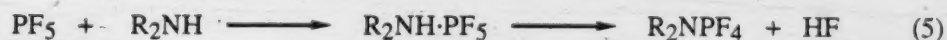
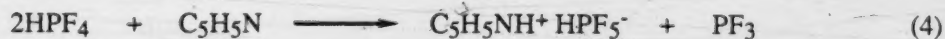
Such d -orbital participation in π back-donation appears to be a reasonable interpretation for the behaviour of these compounds but the question of d -orbital involvement in the σ framework for tetra-, penta-, and hexacoordinate phosphorus compounds remains unanswered.

There are numerous pentavalent phosphorus compounds found in the four- and five-coordinate state. In addition, several examples of hexacoordinate phosphorus anions of the type PX_6^- , which are isoelectronic to the stable neutral sulfur compounds SX_6 , exist. However, neutral compounds containing hexacoordinate phosphorus are not nearly as abundant and were, in fact, until recently unknown. As the chemistry of these unusual compounds is highlighted, one should keep in mind not only the substituent and steric effects, but also the potential role of the vacant $3d$ orbitals in the bonding.

1.5.2 Review of Previous Work

The earliest example of a neutral hexacoordinate phosphorus center was the $\text{Cl}_5\text{P}\cdot\text{py}$ (py = pyridine) adduct mentioned independently by Holmes¹⁰² and Gutmann¹⁰³ in 1954. More detailed accounts of this family of $\text{Cl}_5\text{P}\cdot\text{py}$ compounds followed, including a solid-state ^{31}P NMR study by Dillon.¹⁰⁴ Other Lewis bases such as amines, ethers, and thioethers have been used to attach to the Lewis acid center of phosphorus pentahalides to form these high coordinate phosphorus adducts.^{105,106} In addition, complexes have been formed using alkylphosphines to generate six-coordinate phosphoranes containing a P(V)-P(III) bond.^{107,108}

Several difficulties in the formation of some of these adducts have been reported. If labile hydrogen atoms are present on either the donor or acceptor there is a risk of decomposition by HF elimination to form either anions with six-coordinate phosphorus or neutral molecules with five-coordinate phosphorus, as illustrated by equations (4) and (5).



Many of the adducts with oxygen, sulfur, and phosphorus donors are not highly stable. They will quite often decompose at room temperature in a complex reaction usually generating much more thermally stable species such as PF_6^- (eq.(6)).



The formation of these donor-acceptor adducts is dependent on:

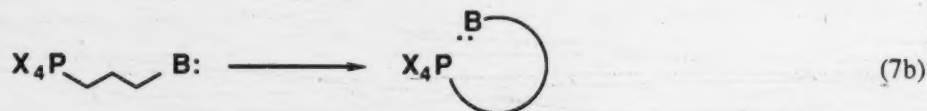
- (a) the nature of the Lewis acid site,
- (b) the nature of the Lewis base site, and
- (c) steric hindrance.

The acceptor ability of the acidic phosphorus center is determined by the number and strength of the electron withdrawing groups around it. For example, in the fluorophosphoranes a decrease in acceptor strength is observed as the number of fluorines decreases. The order $\text{PF}_5 > \text{PhPF}_4 > \text{RPF}_4 > \text{Ph}_2\text{PF}_3 > \text{Ph(R)PF}_3 > \text{R}_2\text{PF}_3$ has been suggested in the recent literature.¹⁰⁹

The ability of the base to donate its electron density also influences the formation of these adducts. For example, both base strength and the ability to form a PF_5 adduct decreases in the same order for this series, $\text{PMe}_3 > \text{PHMe}_2 > \text{PH}_2\text{Me} > \text{PH}_3$, of alkylphosphines.¹⁰⁸

The steric hindrance of the λ^5 -phosphorus center and the incoming Lewis base also influence the formation of these adducts. The amount of physical space around the coordinatively saturated phosphorus is limited. So, for example, while adducts like $\text{F}_5\text{P} \cdot \text{PMe}_3$ are readily prepared, the analogous $\text{F}_5\text{P} \cdot \text{PPh}_3$ is not known.

Most of the neutral hexacoordinate phosphorus compounds prepared to date have been monocyclic phosphoranes. They are most commonly formed from a λ^5 -phosphorane and an organic bidentate ligand. One end of this ligand undergoes a simple substitution with the λ^5 -phosphorane to form a five-coordinate phosphorus compound (eq.(7a)) and the other end of the bidentate ligand acts as a Lewis base and coordinates to the acidic phosphorus center forming the sixth bond in a donor-acceptor interaction similar to the adducts previously discussed (eq.(7b)).



In 1966, Brown and Bladon prepared $\text{F}_4\text{P}(\text{acac})^{110}$, which was the first example of such a neutral monocyclic phosphorane. Subsequent structural characterization showed that it had a distorted octahedral arrangement around the central phosphorus.¹¹¹ Synthesis of other compounds by means of nucleophilic substitution of a λ^5 -phosphorus, accompanied by coordination of a ligand donor center onto the phosphorus, quickly followed. Bidentate ligands such as 8-hydroxyquinolines, 2-aminophenol, urea, benzamidines, carbamates, and thiocarbamates have been used to chelate (usually through N, O, or S atoms) to the phosphorus.

The silylated 8-hydroxyquinoline has been successfully used to chelate several fluorophosphoranes to form a five-membered monocyclic ring and thus create a λ^6 -phosphorus center.¹¹² It has been shown that the tendency to form the six-coordinate center increases as the electronegativity of the other groups on phosphorus increases. Recently, the analogous 2-aminophenol λ^6 -phosphorane, $\text{F}_4\text{P}(\text{NHC}_6\text{H}_4\text{O})_2$, was also reported.¹¹³ The authors note, however, that similar reactions using PhPF_4 or MePF_4 result in HF elimination and formation of only the five-coordinate phosphoranes $\text{PhP}(\text{NHC}_6\text{H}_4\text{O})_2$ and $\text{MeP}(\text{NHC}_6\text{H}_4\text{O})_2$, respectively. This provides an example of the influence of the nature of the ligands around phosphorus on the formation of a hexacoordinate product. Similar reaction trends have been observed for other such monocyclic λ^6 -phosphorus compounds. The series of benzamidine λ^6 -phosphoranes that has been investigated is quite extensive.¹¹⁴ These form four-membered monocyclic rings with an N-C-N bidentate ligand. The stability of this ring is greatly dependent not only on the substituents around phosphorus, but also on those in the N-C-N ligand (Figure 1.5). For example, when R_1 is a phenyl group, formation of a four-membered ring is favoured

and one obtains the λ^6 -phosphorus compound. If, however, the phenyl group (R_1) is replaced with a stronger electron withdrawing group, such as CCl_3 or CF_3 , the ligand becomes monodentate and a λ^5 -phosphorane results.

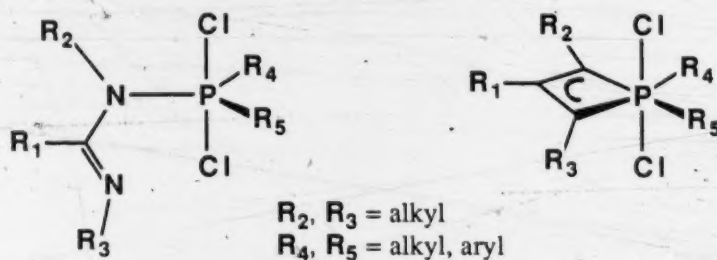
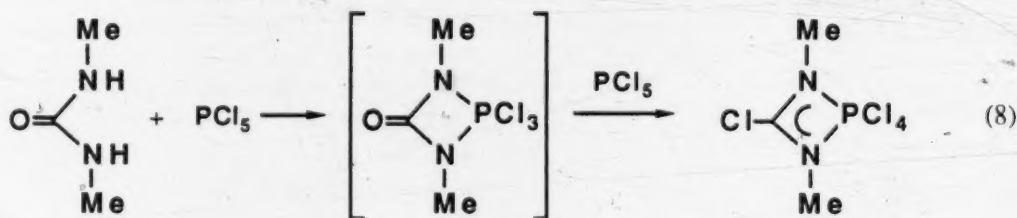


Figure 1.5 Benzamidine λ^5 - and λ^6 -phosphoranes.

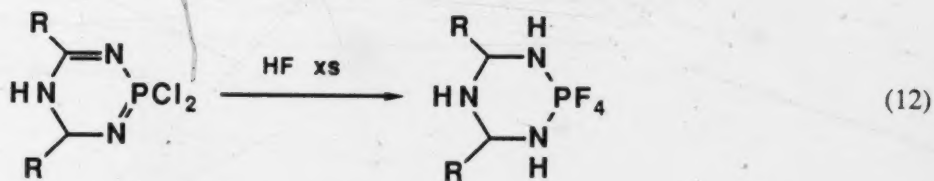
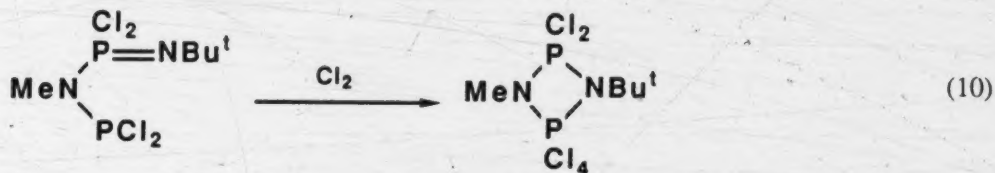
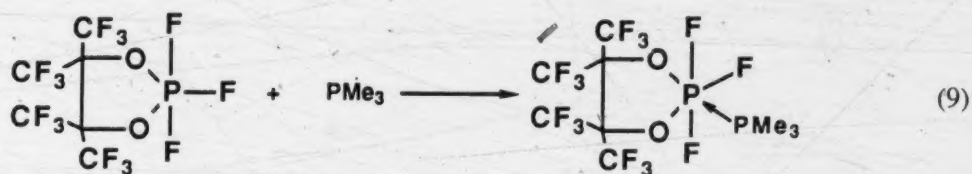
Systems with other four-membered rings forming monocyclic λ^6 -phosphoranes have also been studied. The reaction of PCl_5 with N,N' -dimethylurea produced such a small ring λ^6 -phosphorus compound.^{115,116} Surprisingly, the original compound is not preserved in the final product; rather, the carbonyl function has been transformed. It has been proposed that the reaction proceeds via attachment of a urea ligand to form the λ^5 -phosphorus intermediate which undergoes further chlorination by PCl_5 to form the final product (eq.(8)).



The silylated form of dimethylcarbamate has been used by our group to prepare a series of λ^6 -(carbamato)phosphoranes, which also contain a four-membered monocyclic

ring.^{117,118,119} Kinetic studies indicate that there is opening of this four-membered ring and subsequent exchange of the ligands around phosphorus.¹²⁰ Curiously, these same compounds can also be readily prepared by an apparent insertion of CO₂, COS, or CS₂ into the P-N bond of the λ⁵-dimethylaminophosphorane (X₄PNMe₂). However this insertion reaction is not general.

There are also a few rare examples of monocyclic λ⁶-phosphoranes obtained using more exotic methods, including simple adduct formation of a λ⁵-phosphorane already containing a monocycle (eq.(9)),¹²¹ oxidation of a P(III) to P(V) by chlorine with subsequent ring closing (eq.(10)),¹²² disproportionation of a λ⁵-P(V) ring system induced by steric hindrance (eq.(11)),¹²³ and hydrofluorination of a λ⁴-P(V) ring system (eq.(12)).^{124,125}

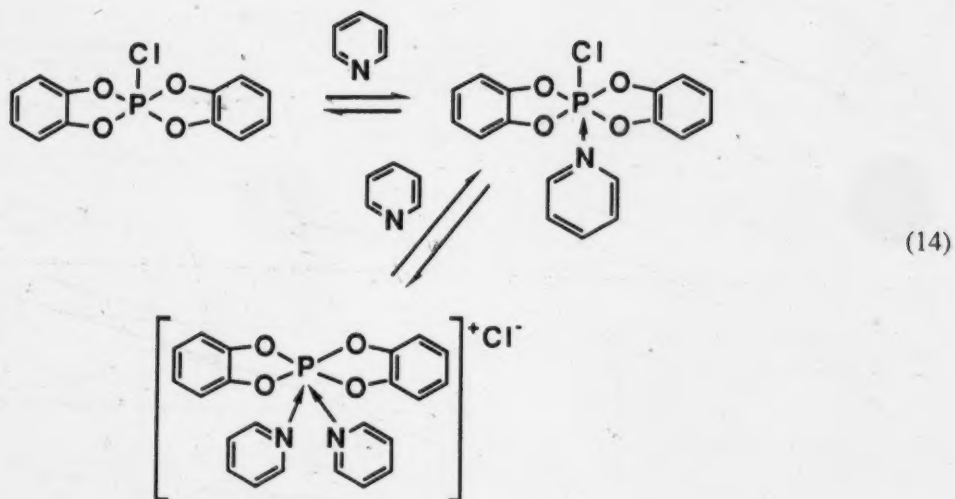


In addition, an unusual rearrangement reaction by addition of a secondary amine, HNR_2 , to obtain a λ^6 -phosphorane was recently reported in the literature (eq.(13)).¹²⁶

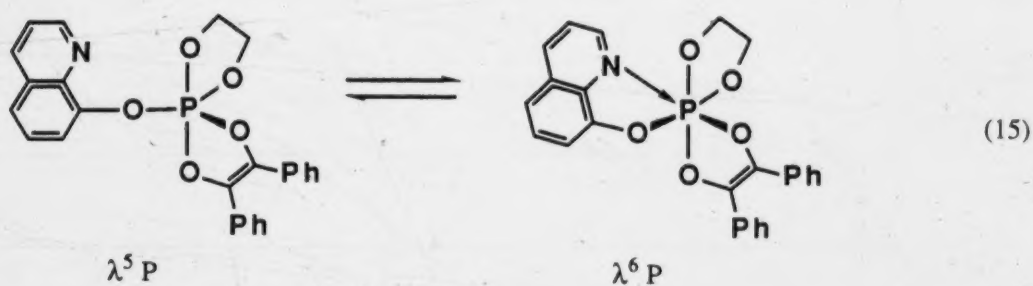


Although the routes to these neutral hexacoordinate compounds are unusual it should be noted that in all cases the final product contains a chelating bidentate ligand coordinated at Lewis base sites (N, O, S, P) to a phosphorus center which is stabilized by electron withdrawing groups.

There are only a few examples of hexacoordinate compounds that are polycyclic or contain more than one bidentate ligand. Most of these compounds are proposed intermediate species usually in a $\lambda^5\text{-P} - \lambda^6\text{-P}$ equilibrium. For example, the bicyclic λ^5 -phosphorus compound (eq.(14)) is in rapid equilibrium with the pyridine adduct.¹²⁷ Eventually the stable cationic λ^6 -phosphorus compound is formed.

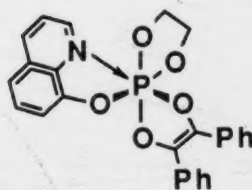


In other cases a λ^5 -P- λ^6 -P equilibrium is observed in which a tricyclic λ^6 -phosphorus is generated by ring closing of the fifth λ^5 -phosphorus ligand. For example:¹²⁸

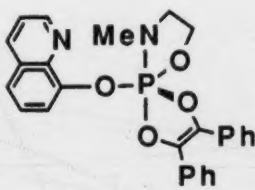


the authors note that a decrease in temperature shifts the equilibrium towards the λ^6 -phosphorus isomer, suggesting that it is thermodynamically more stable. A series of related polycyclic phosphorus compounds has been studied to determine the factors which influence formation of hexacoordinate centers. Like previous researchers, Munoz and coworkers observed that the electron-accepting properties of the substituents at the phosphorus as well as steric effects have a decisive role in determining hexacoordination. For example, if the ethylenedioxy fragment of the hexacoordinate species (31) is modified

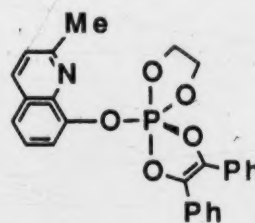
by replacing the O with a NMe group, only the λ^5 -phosphorus is observed (32). That is, the more electron-donating NMe group lowers the Lewis acidity of the phosphorus. If a methyl group is attached to the two position in the 8-hydroxyquinoline ligand, the λ^5 -phosphorus compound is favoured (33).



31

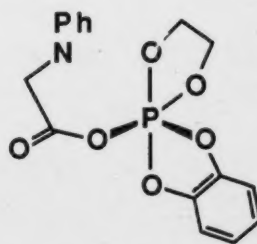


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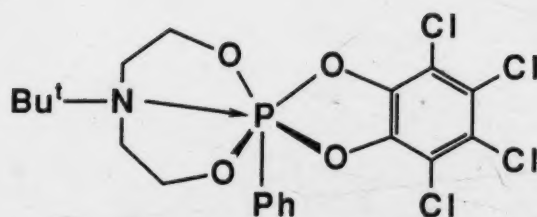
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In addition, Munoz and coworkers note that hexacoordinate structures seem to be stabilized by electron delocalization within the ligands. The 8-hydroxyquinoline ligand, in which greater electron delocalization can be established, favours λ^6 -phosphorus formation (31), compared to the aliphatic nature of the N-phenylglycine ligand, which favours λ^5 -phosphorus formation (34).



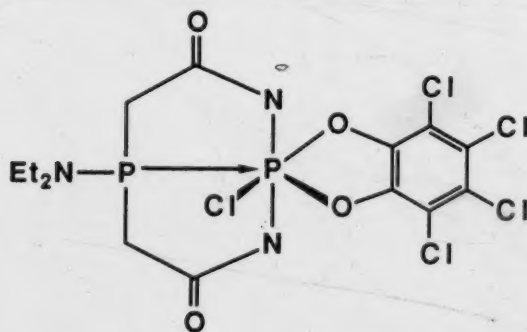
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There are other rare polycyclic λ^6 -phosphorus compounds that are worth noting. The use of (ONO) tridentate ligands has been reported, in which six coordination is obtained by the formation of a transannular N-P bond (35).^{129,130}



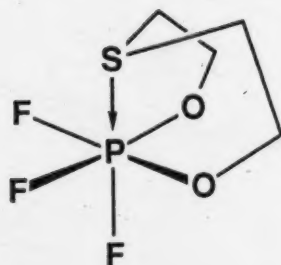
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The hexacoordinate species was found to be in equilibrium with the five-coordinate species, resulting in an inseparable mixture of the λ^5 -phosphorus and λ^6 -phosphorus compounds. In addition, a (NPN) tridentate ligand has been used to prepare a mixed-valence diphosphorus P(V)-P(III) compound, which is six-coordinate (36).¹³¹ In this case a P(V)-P(III) transannular bond forms to complete the hexacoordination.



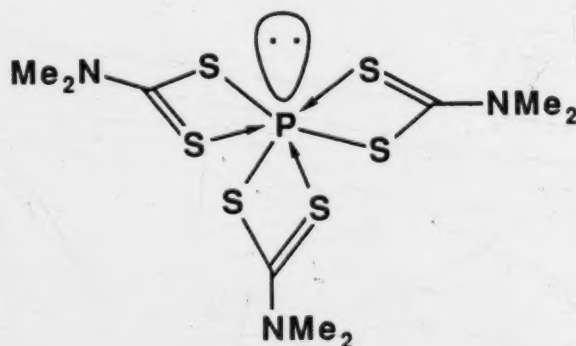
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More recently an (OSO) tridentate ligand has been used to prepare this bicyclic phosphorus compound containing a P-S bond (37).¹¹³



37

Finally, both the preparation¹³² and structure¹³³ of a polycyclic phosphorus compound using dithiocarbamate ligands have been reported. Similar to the trisdithiocarbamate arsenic compound previously discussed (24), this tris(dithiocarbamato)phosphine (38) is also hexacoordinate, with three short P-S bonds (2.178 Å) and three longer P-S bonds (2.966 Å).



38

It has been suggested that this compound can be viewed as a pseudo-heptacoordinate species, where the lone pair of electrons represents the seventh coordination site.¹³³

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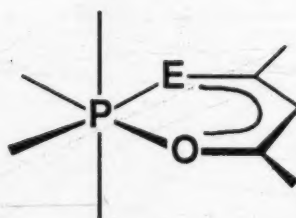
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CHAPTER II

ACETYLACETONATE DERIVATIVES OF HEXACOORDINATE PHOSPHORUS(V)



2.1 Introduction

In this chapter the synthesis and characterization of a series of acetylacetonate (acac) neutral hexacoordinate phosphorus compounds (see Figure 2.1) with the general formula $F_{4-n}(CF_3)_nP(acac)$ ($n = 0-3$) and $CH_3(CF_3)_3P(acac)$ are described. The prototypical member of this system, $F_4P(acac)$, was prepared in 1966¹ and was structurally characterized in 1978.² These compounds (1-5) each contain one symmetric acetylacetonate ligand forming neutral hexacoordinate phosphoranes with a six-membered chelating ring. The preparation and characterization by spectroscopic techniques was initially carried out by Neil Burford.³ The x-ray crystallographic structure, coupled with multinuclear NMR, infrared, mass, and ultraviolet spectroscopic data of these compounds (1-5), is reported in this thesis.

In addition, the synthesis and characterization by multinuclear NMR spectroscopy of (4-aminopent-3-en-2-onato)tris(tri-fluoromethyl)methyl-phosphorus(V) [$CH_3(CF_3)_3P$ -(aminoacac) (6)] and (4-methylamino-pent-3-en-2-onato)tris(trifluoromethyl)methyl-phosphorus(V) [$CH_3(CF_3)_3P$ (N-methyl-aminoacac) (7)] are described (Figure 2.1). These compounds (6 and 7) contain one unsymmetric ligand and form a neutral λ^6 -phosphorane analogous to 5. The lower symmetry of 6 and 7 enables complete structural characterization by multinuclear NMR.

Finally, using a gaseous high dilution reaction mixture of PF_5 and $(CH_3)_3Si(O_2CN(CH_3)_2)$, the synthesis of $F_4P(O_2CN(CH_3)_2)$ (8) (Figure 2.1) and its characterization by ^{19}F and ^{31}P NMR spectroscopies are also described.

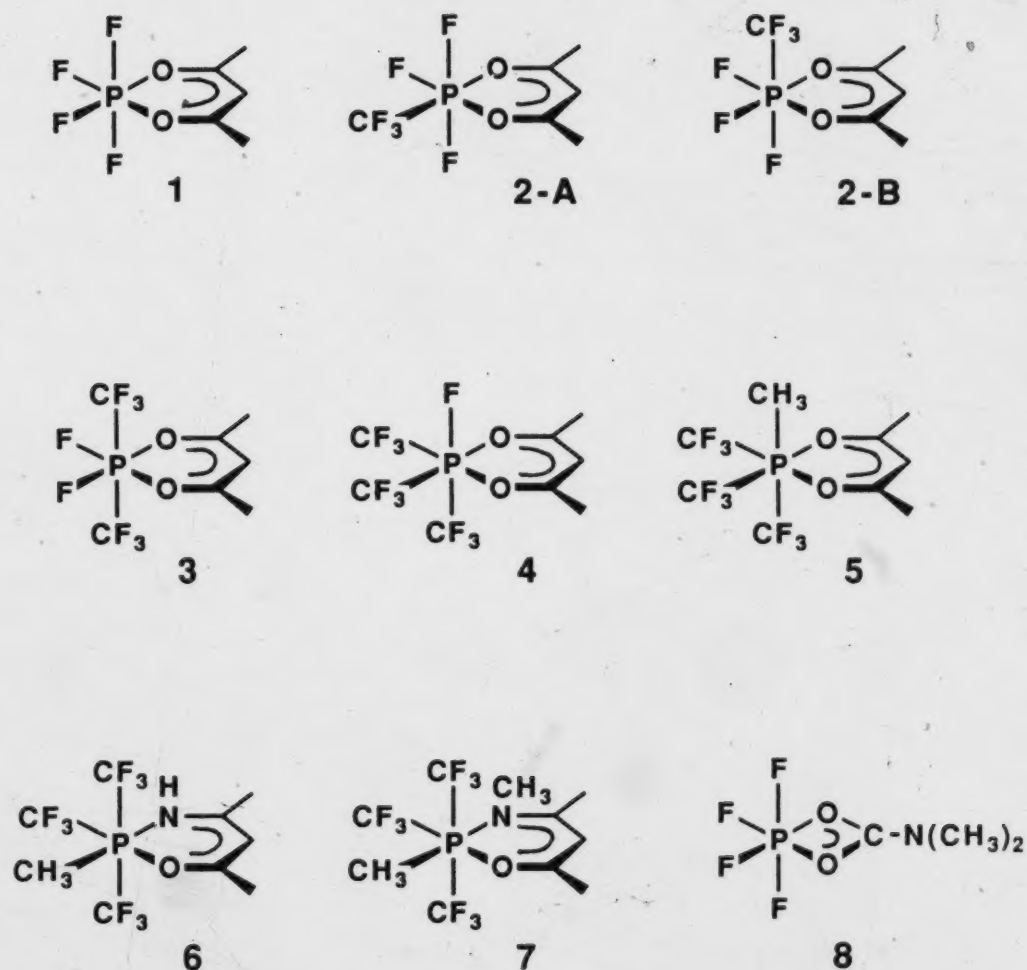


Figure 2.1 Six-coordinate $F_{4-n}(CF_3)_nP(acac)$ ($n = 0-3$), $CH_3(CF_3)_3P(acac)$ (1-5), $CH_3(CF_3)_3P(aminoacac)$ (6), $CH_3(CF_3)_3P(methylaminoacac)$ (7), and $F_4P(N,N\text{-dimethylcarbamate})$ (8).

2.2 Experimental

2.2.1 General Procedures

All reactions were carried out in sealed tubes, and standard vacuum line techniques were employed for the manipulation of volatile materials. Diethyl ether was dried before use by distillation over LiAlH_4 and chloroform by distillation over P_2O_5 . All of the phosphoranes used were prepared by literature methods.^{4,5} Sodium acetylacetonate was prepared from NaOH and acetylacetone in ethanol, and acetylacetone (Aldrich) was used as received. Both the aminoacetylacetone and the N-methylaminoacetylacetone were prepared according to literature methods from acetylacetone and a 40% aqueous solution of the respective amine.⁶ Infrared spectra were obtained as Nujol mulls of the solid samples with CsI plates on a Perkin-Elmer 457 grating spectrometer. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. The NMR spectra were recorded on solutions of the compound in CD_2Cl_2 or CDCl_3 . The ^1H NMR spectra were measured on a Bruker WP-80 instrument in the continuous-wave mode, and the chemical shifts were measured relative to an external Me_4Si sample. Both ^{19}F and ^{31}P NMR spectra were recorded on a Bruker WP-400 spectrometer at 376.4 and 161.98 MHz, respectively. Chemical shifts were measured with respect to the heteronuclear ^2D lock signal and converted to the CFCl_3 scale in the case of ^{19}F and the H_3PO_4 scale in the case of ^{31}P by means of the appropriate conversion factors.

2.2.2 Preparation of (Pentane-2,4-dionato)fluorophosphoranes (1-5)

The phosphorus compounds with the general formula $F_{4-n}(CF_3)_nP(acac)$ ($n = 0-3$) (1-4) and $CH_3(CF_3)_3P(acac)$ (5), were prepared by the literature methods.¹⁻³

2.2.3 Preparation of (4-aminopent-3-en-2-onato)tris(trifluoromethyl)methylphosphorus(V) (6)

A sample of aminoacetylacetone (0.0772 g, 0.780 mmol) and $CH_3(CF_3)_3PCl$ (0.151 g, 0.524 mmol) were combined under vacuum with 10 mL of $CHCl_3$ in a sealed tube. As the reaction vessel was slowly warmed to room temperature, a pale yellow precipitate was formed. The precipitate was filtered out with a glass frit and the remaining solution was characterized by ^{31}P and ^{19}F NMR spectroscopy (see Table 2.7).

2.2.4 Preparation of (4-methylaminopent-3-en-2-onato)tris(trifluoromethyl)methylphosphorus(V) (7)

A sample of (methylamino)acetylacetone (0.269 g, 2.38 mmol) and $CH_3(CF_3)_3PCl$ (0.505 g, 1.75 mmol) were combined under vacuum with 10 mL of $CHCl_3$ in a sealed tube. Upon warming the solution slowly to room temperature a white precipitate formed. The precipitate was filtered out with a glass frit and the remaining solution was characterized by ^{31}P and ^{19}F NMR spectroscopy (see Table 2.7).

2.2.5 Preparation of tetrafluoro(N,N-dimethylcarbamato)-phosphorus(V) (8)

A sample of PF_5 (55 mm Hg, 183 mL, 0.54 mmol) was distilled into section A of the glass reaction vessel shown in Figure 2.2. Section A was sealed by closing tap D and the vessel was opened by removing the large glass bulb of section C. An excess sample of $(\text{CH}_3)_3\text{Si}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ (0.52 g, 3.23 mmol) was placed in sidearm B of the vessel by a syringe. The reaction vessel was resealed by replacing C and the $(\text{CH}_3)_3\text{Si}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ in sidearm B was degassed three times using a freeze-thaw cycle. With taps D and E closed, sidearm B was gently warmed to vapourize the $(\text{CH}_3)_3\text{Si}(\text{O}_2\text{CN}(\text{CH}_3)_2)$. Then, tap D was opened to allow the PF_5 gas to mix in high dilution with the $(\text{CH}_3)_3\text{Si}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ vapour in the large bulb (C). A white film formed immediately on the inside wall of C. The gases in the vessel were left to react at room temperature for three hours. The infrared spectrum of a vapour sample from the reaction vessel confirmed the formation of $(\text{CH}_3)_3\text{SiF}$. The remaining volatile materials were pumped away to leave a white solid, which was characterized by ^{19}F and ^{31}P NMR spectroscopies.

2.2.6 X-ray Data Collection and Structure Solution for Compounds 3 and 4⁷

Clear colorless crystals of both compounds were obtained as described above. Data were collected on an Enraf-Nonius CAD4 diffractometer on which the crystals were cooled to -65°C by using a cold air stream apparatus (F.T.S. Systems). Collection of data for 3 and 4, and structure solution of 3 was carried out by Dr. R.G. Ball. Structure solution of 4 was carried out by the author under the supervision of Professor M. Cowie. Compound 3 crystallized poorly so it was extremely difficult to get crystals of suitable X-ray quality, and the crystal ultimately chosen, although the best of a large number sampled, still did not

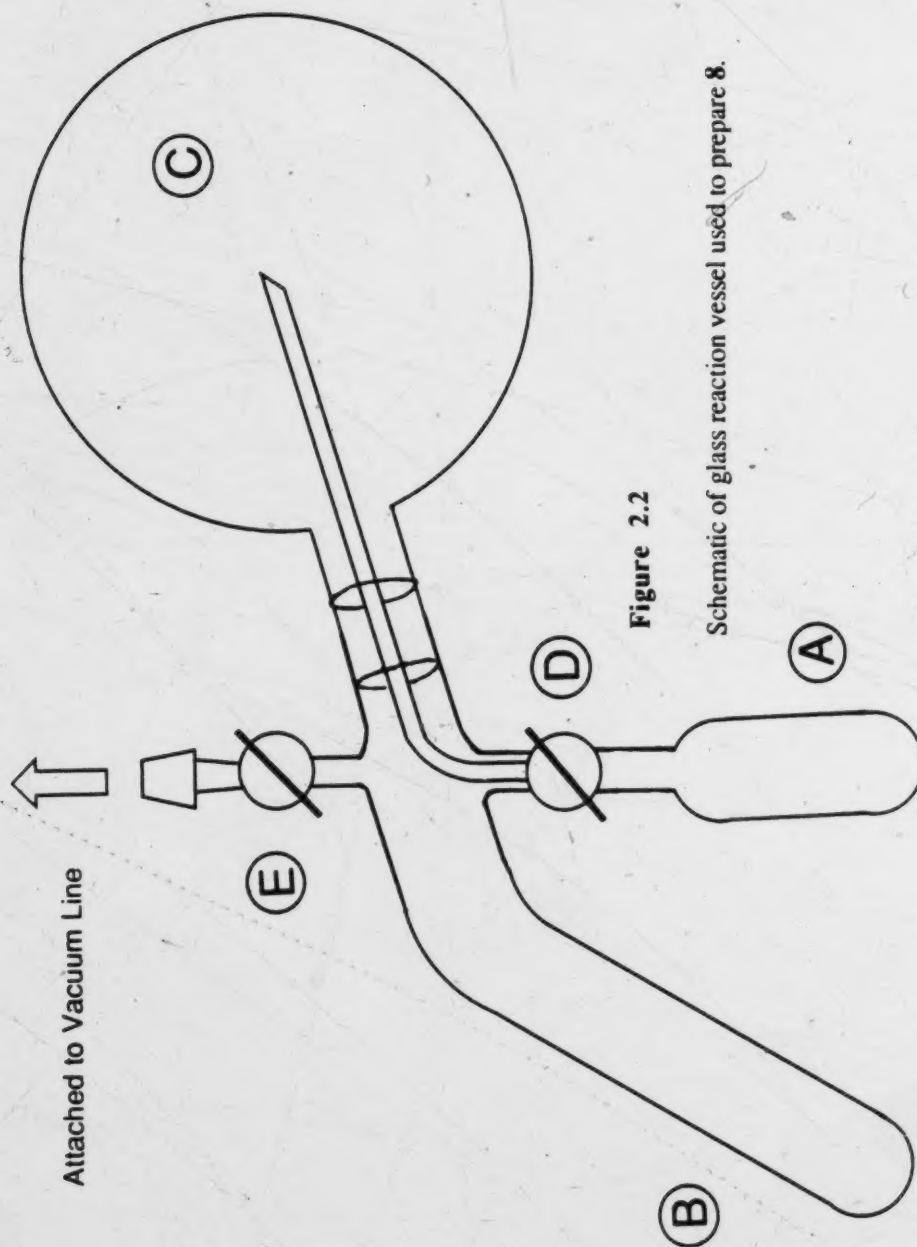


Figure 2.2

Schematic of glass reaction vessel used to prepare 8.

diffract X-rays well.⁸ As a result the number of observed reflections was low and the final residuals were high (see Table 2.1 for crystal data and intensity collection details).

Intensity measurements were made with graphite-monochromated Mo K α radiation. The automatic peak search and reflection indexing programs,⁹ in conjunction with a cell reduction program, established the crystal systems, and the systematic absences unambiguously established the space groups¹⁰ as *Pbca* (*0kl*, *k* odd; *h0l*, *l* odd; *hk0*, *h* odd) for compound 3 and *P2₁/c* (*h0l*, *l* odd; *0k0*, *k* odd) for compound 4. Cell constants were obtained from a least-squares refinement of the setting angles of 20 reflections having 2θ between 11 and 26° for compound 3 and 25 reflections having 2θ between 12 and 20° for compound 4.

The intensity data were collected by using an ω - 2θ scan with variable scan speeds chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 60 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1 - α_2 wavelength dispersion. Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Two reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. For both compounds the standards showed variations of up to 11%; however, these variations were not uniform over the two standards collected for each compound and so no correction was applied. These fluctuations were probably due to slight crystal movement caused by the flow of cold air from the cooling apparatus.

The data were corrected for Lorentz and polarization effects¹¹ but not for absorption, owing to the very small linear absorption coefficients. Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections.

Both structures were solved with MULTAN¹² (incorporating the RANTAN option for compound 3). This yielded the positions of most non-hydrogen atoms; those remaining were located by the usual combination of least-squares refinement and difference Fourier

Table 2.1 Crystal Data and Details of Intensity Collection

	F ₂ (CF ₃) ₂ P(acac) (3)	F(CF ₃) ₃ P(acac) (4)
mol formula	C ₇ H ₇ F ₈ O ₂ P	C ₈ H ₇ F ₁₀ O ₂ P
fw	306.09	356.10
cryst shape	plate	monoclinic prism
cryst size (mm)	0.07 x 0.26 x 0.28	0.28 x 0.30 x 0.41
systematic absences	0 <i>kl</i> (<i>k</i> odd), <i>h</i> 0 <i>l</i> (<i>l</i> odd), <i>hk</i> 0 (<i>h</i> odd)	<i>h</i> 0 <i>l</i> (<i>l</i> odd), 0 <i>k</i> 0 (<i>k</i> odd)
space group	orthorhombic, <i>Pbca</i> (No. 61)	monoclinic, <i>P</i> 2 ₁ / <i>c</i> (No. 14)
temp (°C)	- 65	- 65
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
unit cell parameters		
<i>a</i> (Å)	12.323 (4)	10.218 (1)
<i>b</i> (Å)	22.871 (5)	8.822 (3)
<i>c</i> (Å)	7.505 (5)	13.930 (7)
β (deg)		107.21 (3)
Volume (Å ³)	2115	1199
<i>Z</i>	8	4
ρ _{calcd} (g cm ⁻³)	1.922	1.977
linear abs coeff (μ, cm ⁻¹)	3.57	3.52
max 2θ reflections		
collected (deg)	54.00	52.00
index range	(+ <i>h</i> , + <i>k</i> , + <i>l</i>)	(+ <i>h</i> , + <i>k</i> , ± <i>l</i>)
takeoff angle (deg)	3.00	3.00
detector aperture (mm)	2.40 (horiz), 4.00 (vert)	2.40 (horiz), 4.00 (vert)
cryst to detector dist (mm)	205	205
scan type	ω - 2θ	ω - 2θ
scan rate (deg min ⁻¹)	10.1-1.5	10.1-1.3
scan width (deg)	0.80 + 0.35 tanθ	0.70 + 0.35 tanθ
total reflections collected	2666	2685
no. of indep reflections	2302	2593
no. of observs (<i>I</i> > 3σ(<i>I</i>))	907	2038
no. of variables	142	190
final <i>R</i> , <i>R</i> _w , GOF ^a	0.090, 0.105, 3.09	0.047, 0.070, 2.72

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$;

 $GOF = [\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$

techniques. In compound **4**, the hydrogen atoms were located and were input to the least-squares cycles as fixed contributions in their idealized positions. These positions were obtained from the observed ones by assuming the appropriate hybridization of their attached carbon atom and using C-H distances of 0.95 Å. In compound **3** not all of the hydrogens were obvious and so none were included in the subsequent refinements.

Refinement was carried out with full-matrix least-squares techniques, minimizing the function $\sum w (|F_o| - |F_c|)^2$, with $w = 4F_o^2 / \sigma^2(F_o^2)$. The neutral atom scattering factors¹³ and the anomalous dispersion terms for all non-hydrogen atoms¹⁴ were obtained from the usual sources. As refinement of compound **3** progressed, it became obvious that the two CF₃ groups were rotationally disordered such that, for each group, there was one major occupancy and two equally weighted minor occupancies. In the final model the three primary fluorine positions, on each CF₃ group, were assigned half-occupancies and were refined isotropically. The remaining six fluorine positions, corresponding to two CF₃ orientations, were assigned isotropic thermal parameters and occupancies of 0.25. These six minor positions were constrained to "ride" on the C atom of the group.

Analyses of F_o vs. F_c for both structures showed no unusual trends. The highest peak in the final difference Fourier map was 0.8(2) e Å⁻³ for compound **3** and 0.4(1) e Å⁻³ for compound **4**. The final R values for **3** and **4** were 0.090 and 0.047, respectively.

The positional and isotropic thermal parameters for compounds **3** and **4** are given in Tables 2.2 and 2.3, respectively. Additional information is available in the full reports.⁷

Table 2.2 Positional^a and Thermal Parameters for F₂(CF₃)₂P(acac) (3)

atom	x	y	z	B, ^b Å ²
P	343.6 (2)	125.6 (1)	204.6 (4)	1.90 (4) ^{c, d}
F(7)	414.3 (5)	89.9 (3)	349.4 (8)	2.8 (2) ^c
F(8)	281.8 (5)	161.7 (3)	355.3 (8)	2.7 (2) ^c
F(1)	169	70	80	2.5 (2)
F(2)	178.3 (9)	69.0 (5)	369 (2)	2.2 (2)
F(3)	280 (1)	10.6 (5)	213 (2)	2.7 (2)
F(4)	516.4 (9)	185.5 (5)	342 (1)	1.9 (2)
F(5)	522.1 (9)	181.3 (5)	60 (1)	2.1 (2)
F(6)	406.6 (9)	239.7 (5)	176 (1)	2.1 (2)
F(1) ^e	143	82	143	4.7 (7)
F(2)'	218	50	385	4.9 (7)
F(3)'	272	18	127	3.8 (6)
F(1)''	150	82	309	5.4 (7)
F(2)''	279	17	294	4.2 (6)
F(3)''	204	50	51	4.2 (6)
F(4)'	544	170	283	11 (2)
F(5)'	484	196	23	3.4 (5)
F(6)'	413	234	263	3.3 (5)
F(4)''	548	166	119	5.0 (7)
F(5)''	417	230	94	6 (1)
F(6)''	476	205	356	4.9 (7)
O(1)	413.2 (5)	84.8 (4)	44.7 (9)	2.3 (2) ^c
O(2)	264.3 (5)	163.9 (3)	52.4 (9)	2.0 (2) ^c
C(1)	238.3 (8)	67.0 (5)	218 (2)	2.6 (2) ^c
C(2)	448.2 (9)	185.8 (5)	193 (2)	2.9 (3) ^c
C(3)	407.1 (9)	88.8 (5)	-132 (1)	2.1 (2) ^c
C(4)	486 (1)	52.0 (5)	-227 (2)	3.4 (3) ^c
C(5)	335 (1)	124.4 (6)	-218 (1)	2.8 (2) ^c
C(6)	264.7 (9)	161.1 (5)	-124 (1)	2.0 (2) ^c
C(7)	181.8 (7)	197.8 (4)	-209 (1)	3.0 (3) ^c

^a Values x 10³.^b The equivalent isotropic thermal parameter given by $B = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$.^c This atom was refined anisotropically.^d The numbers in parentheses are estimated standard deviations in the least significant digits. Those parameters without an esd were not refined.^e The primed and double-primed F atoms are the two additional sets of disordered CF₃ groups having minor occupancies (see Section 2.2 Experimental).

Table 2.3 Positional and Thermal Parameters for F(CF₃)₃P(acac) (4)

atom	x	y	z	B, ^a Å ²
P	0.73365 (5) ^b	0.00038 (6)	0.25619 (4)	1.52 (1)
F(1)	0.5933 (1)	0.0510 (2)	0.2776 (1)	2.17 (3)
F(2)	0.9538 (1)	0.0591 (2)	0.1874 (1)	3.08 (3)
F(3)	0.9137 (2)	-0.1782 (2)	0.1914 (1)	3.06 (3)
F(4)	1.0083 (2)	-0.0584 (2)	0.3289 (1)	3.10 (3)
F(5)	0.6476 (2)	-0.2752 (2)	0.1641 (1)	3.63 (4)
F(6)	0.6776 (2)	-0.1070 (2)	0.0627 (1)	3.08 (3)
F(7)	0.5006 (2)	-0.0953 (2)	0.1144 (1)	3.76 (4)
F(8)	0.7881 (2)	-0.1037 (2)	0.4513 (1)	3.84 (4)
F(9)	0.8341 (2)	-0.2689 (2)	0.3538 (1)	3.02 (3)
F(10)	0.6268 (2)	-0.2218 (2)	0.3454 (1)	3.57 (3)
O(1)	0.8232 (2)	0.1253 (2)	0.3499 (1)	1.98 (3)
O(2)	0.7066 (2)	0.1412 (2)	0.1637 (1)	1.81 (3)
C(1)	0.9112 (2)	-0.0472 (3)	0.2399 (2)	2.04 (4)
C(2)	0.6360 (3)	-0.1264 (3)	0.1443 (2)	2.35 (5)
C(3)	0.7484 (2)	-0.1557 (3)	0.3572 (2)	2.13 (4)
C(4)	0.7992 (3)	0.2703 (3)	0.3537 (2)	1.95 (5)
C(5)	0.8647 (2)	0.3401 (3)	0.4540 (2)	2.81 (4)
C(6)	0.7258 (2)	0.3511 (3)	0.2711 (2)	2.10 (4)
C(7)	0.6882 (2)	0.2849 (3)	0.1772 (2)	1.84 (4)
C(8)	0.6302 (3)	0.3725 (3)	0.0828 (2)	2.64 (5)
H(1)C(6)	0.700	0.453	0.279	3.11 ^c
H(1)C(4)	0.843	0.445	0.452	3.81 ^c
H(2)C(4)	0.830	0.291	0.502	3.81 ^c
H(3)C(4)	0.961	0.328	0.472	3.81 ^c
H(1)C(8)	0.585	0.460	0.097	3.63 ^c
H(2)C(8)	0.701	0.402	0.055	3.63 ^c
H(3)C(8)	0.566	0.310	0.036	3.63 ^c

^a The equivalent isotropic thermal parameter is given by $B = (8\pi^2/3)(U_{11}/\sin^2\beta + U_{22} + U_{33}/\sin^2\beta + 2U_{13}/\sin^2\beta)$.

^b Numbers in parentheses are estimated standard deviations in the least significant digits.

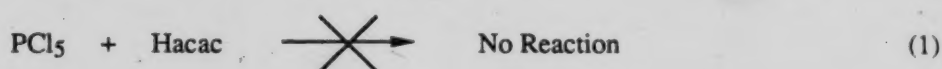
^c This atom was not refined.

2.3 Results and Discussion

As outlined in Chapter 1 (Section 1.5), the formation of these chelated neutral hexacoordinate phosphorus compounds is dependent on:

- (1) the nature of the Lewis acid;
- (2) the nature of the Lewis base; and
- (3) steric hindrance.

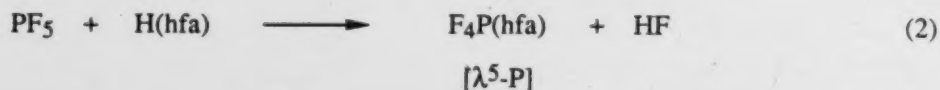
Since the seemingly facile preparation of $F_4P(acac)$, in 1966, by a simple substitution reaction, the number of analogous compounds has been extremely limited. This is in part due to the limitations imposed on the reactants required to form a neutral compound with a six-coordinate center. For example, the phosphorus must be a strong Lewis acid. This is dependent on the number and strength of the electron withdrawing substituents on the phosphorus atom. While PF_5 and acetylacetone react readily at room temperature to form **1**, the analogous reaction of PCl_5 with acetylacetone does not occur (eq.(1)).



The lower electronegativity of a CF_3 group versus F indicates the Lewis acid strength of the phosphorus center increases in the series: $CH_3(CF_3)_3PF < (CF_3)_3PF_2 < (CF_3)_2PF_3 < (CF_3)PF_4 < PF_5$.

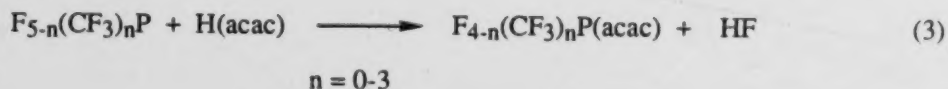
The nature of the ligand used is equally important to formation of these compounds. If the Lewis base is weak, hexacoordination of the phosphorus is not readily achieved. For example, the basicity at the oxygen sites in hexafluoroacetylacetone [$H(hfa)$] is lower than $Hacac$, because of the effect of strongly electron withdrawing CF_3 groups. A compound containing a five-coordinate phosphorus atom forms, as evidenced by ^{31}P NMR

spectroscopy, when PF_5 reacts with H(hfa) (eq.(2)), instead of a compound containing a six-coordinate phosphorus analogous to **1**.



In addition, H(hfa) will not displace *acac* when combined with **1** and H(hfa) will not displace the *N,N*-dimethylcarbamate ligand when combined with $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$, which suggest that the more basic *acac* and carbamate ligands are preferred over *hfa* for forming compounds with hexacoordinate phosphorus centers.

Finally, steric hindrance can influence the formation of λ^6 -phosphorus centers. The (trifluoromethyl)fluorophosphoranes, except $\text{CH}_3(\text{CF}_3)_3\text{PF}$, react readily with acetylacetone at room temperature, undergoing single substitution of fluorine at the phosphorus center (eq.(3)) to form a hexacoordinated phosphorane with a bidentate dione ligand.



The NMR spectra (Table 2.7) of the resultant reaction mixtures show the λ^6 -phosphorane to be the primary component in all cases.³ The lack of reaction in the tetraalkyl case suggests that these reactions proceed via an $\text{S}_{\text{N}}2$ process first forming a six-coordinate intermediate which subsequently eliminates HF . The λ^5 -(tetraalkyl)phosphorane is more sterically hindered than the other λ^5 -phosphoranes used, so a mechanism involving a λ^6 -phosphorus intermediate is not favoured. Using an analogous λ^5 -phosphorane with a better leaving group, such as chlorine (instead of fluorine), could favour an $\text{S}_{\text{N}}1$ mechanism, which would circumvent the problem of steric hindrance of the intermediate. (A detailed illustration and discussion of steric hindrance is presented later in Chapter 3). The tetraalkyl derivative containing a six-coordinate phosphorus was prepared in almost

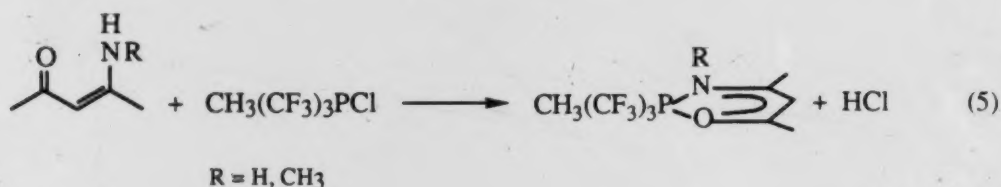
quantitative yield (according to NMR) from $\text{CH}_3(\text{CF}_3)_3\text{PCl}^{15}$ and sodium acetylacetonate ($\text{Na}(\text{acac})$) (eq.(4)),³



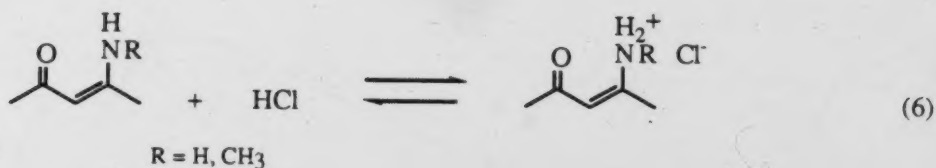
but the isolated yield was poor because of the high solubility of the product. Reactions of the other fluorophosphoranes with sodium acetylacetonate were complex, and only relatively low yields of the hexacoordinate species were obtained. This may be due to secondary or tertiary substitution reactions, a process that cannot occur with the tetraalkyl derivative. The (pentane-2,4-dionato)phosphorus(V) compounds are all air-stable, moisture-sensitive, colorless crystalline solids with sharp melting points except for the isomeric mixture of 2. Unlike the carbamate derivatives, they were insufficiently volatile for purification by sublimation, but were successfully recrystallized from a variety of organic solvents.

Although there is a possibility of two isomers in most cases, and three in the case of $\text{F}_2(\text{CF}_3)_2\text{P}(\text{acac})$, all of the reactions with acetylacetonate, except that involving CF_3PF_4 , gave only one specific structural isomer according to NMR spectra. The crystal and molecular structures of two compounds, $\text{F}_2(\text{CF}_3)_2\text{P}(\text{acac})$ (3) and $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ (4), were determined in order to unambiguously establish their solid-state geometries.

Both the aminoacac and (methylamino)acac ligands react readily with $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ at room temperature, eliminating HCl (eq.(5)).



However, the HCl which is eliminated reacts with these ligands (in equilibrium) to form very stable ammonium chloride salts (eq.(6)).



Hence, crystals of **6** and **7** could not be obtained. (The ³¹P NMR spectra indicate 70-76% of **6** and **7** in solution) Other bases, such as NEt₃, were used in an attempt to scavenge the HCl in solution, but this resulted instead in the formation of CH₃(CF₃)₃ClP·NEt₃ adducts. Perhaps the modification of the aminoacac and (methylamino)acac ligands to the silylated forms (similar to the pyridine compounds of Chapter 4) would eliminate the problem caused by HCl generation.

Because of the lower symmetry of these aminoacac and (methylamino)acac ligands, **6** and **7** can be completely structurally characterized in solution by multinuclear NMR spectroscopy (see Table 2.7). The benefits of using unsymmetrical ligands in preference to symmetrical ligands, such as the carbamates and acetylacetonates, is demonstrated here. This will be seen again in Chapter 4, where a series of unsymmetrical pyridine based compounds is discussed.

2.3.1 Structure of F₂(CF₃)₂P(acac) (**3**)

Compound **3** has an octahedral geometry about phosphorus (Figure 2.3). The two mutually cis fluorine atoms and the acac chelate occupy "radial" positions and define the central plane of the molecule. The two CF₃ groups occupy mutually trans axial positions relative to this central plane, a position that would minimize steric interaction between the bulkiest substituents in the molecule. Relevant metrical parameters for **3** are given in Tables 2.4 and 2.5. Except for the rotational disorder exhibited by the CF₃ groups, as noted

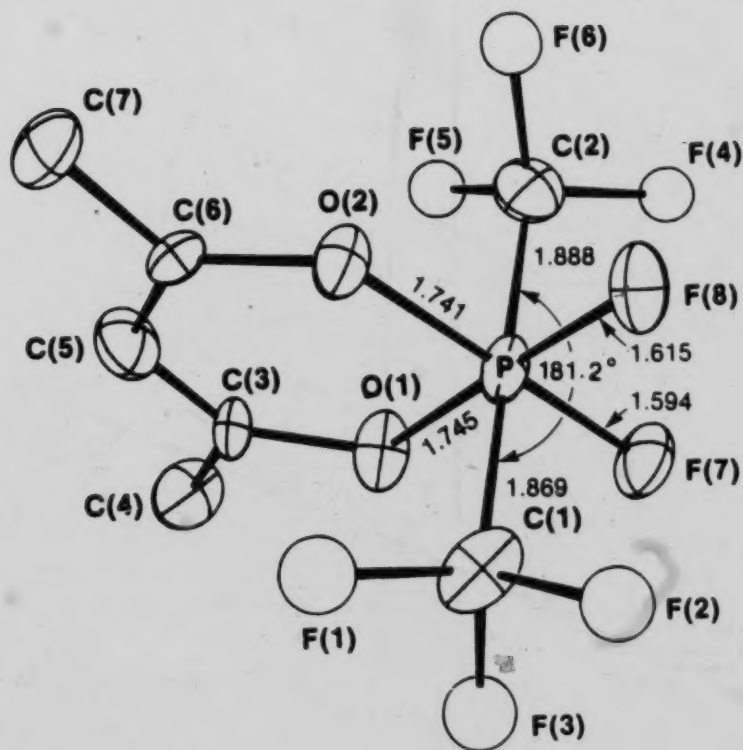


Figure 2.3

Perspective drawing of $\text{F}_2(\text{CF}_3)_2\text{P}(\text{acac})$ (3) showing the numbering scheme. Thermal ellipsoids are shown at the 50% level. For the disordered CF_3 groups only the set of fluorine atoms having the major occupancy is shown. Structure courtesy Dr. R.G. Ball, Structure Determination Laboratory, University of Alberta.

Table 2.4 Bond Distances^a for F₂(CF₃)₂P(acac) (3) and F(CF₃)₃P(acac) (4)

atom 1	atom 2	dist	atom 1	atom 2	dist
F ₂ (CF ₃) ₂ P(acac) (3)					
P	F(7)	1.615 (4) ^b	C(1)	F(2)	1.35 (1)
P	F(8)	1.594 (4)	C(1)	F(3)	1.39 (1)
P	O(1)	1.745 (5)	C(2)	F(4)	1.39 (1)
P	O(2)	1.741 (5)	C(2)	F(5)	1.36 (1)
P	C(1)	1.869 (8)	C(2)	F(6)	1.34 (1)
P	C(2)	1.888 (8)	C(3)	C(4)	1.47 (1)
O(1)	C(3)	1.328 (3)	C(3)	C(5)	1.37 (1)
O(2)	C(6)	1.323 (6)	C(5)	C(6)	1.39 (1)
C(1)	F(1)	1.347 (1)	C(6)	C(7)	1.470 (9)
F(CF ₃) ₃ P(acac) (4)					
P	F(1)	1.612 (1) ^b	F(7)	C(2)	1.350 (2)
P	O(1)	1.746 (1)	F(8)	C(3)	1.334 (2)
P	O(2)	1.752 (1)	F(9)	C(3)	1.338 (2)
P	C(1)	1.940 (1)	F(10)	C(3)	1.338 (2)
P	C(2)	1.938 (2)	O(1)	C(4)	1.306 (2)
P	C(3)	1.942 (2)	O(2)	C(7)	1.304 (2)
F(2)	C(1)	1.339 (2)	C(5)	C(4)	1.493 (2)
F(3)	C(1)	1.343 (2)	C(4)	C(6)	1.373 (2)
F(4)	C(1)	1.343 (2)	C(6)	C(7)	1.379 (2)
F(5)	C(2)	1.340 (2)	C(7)	C(8)	1.489 (2)
F(6)	C(2)	1.337 (2)			

^a In angstroms.^b Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2.5 Bond Angles^a for F₂(CF₃)₂P(acac) (3) and F(CF₃)₃P(acac) (4)

atom 1	atom 2	atom 3	angle
F ₂ (CF ₃) ₂ P(acac) (3)			
F(7)	P	F(8)	92.4 (2) ^b
F(7)	P	O(1)	85.8 (2)
F(7)	P	O(2)	178.4 (3)
F(7)	P	C(1)	88.6 (3)
F(7)	P	C(2)	91.8 (3)
F(8)	P	O(1)	178.2 (3)
F(8)	P	O(2)	86.3 (2)
F(8)	P	C(1)	90.1 (3)
F(8)	P	C(2)	88.8 (3)
O(1)	P	O(2)	95.4 (2)
O(1)	P	C(1)	89.7 (3)
O(1)	P	C(2)	91.4 (3)
O(2)	P	C(1)	90.4 (3)
O(2)	P	C(2)	89.2 (3)
C(1)	P	C(2)	178.8 (4)
P	O(1)	C(3)	128.4 (5)
P	O(2)	C(6)	128.9 (5)
P	C(1)	F(1)	111.3 (5)
P	C(1)	F(2)	113.7 (6)
P	C(1)	F(3)	114.3 (5)
F(1)	C(1)	F(2)	107.0 (6)
F(1)	C(1)	F(3)	105.1 (7)
F(2)	C(1)	F(3)	104.8 (8)
P	C(2)	F(4)	111.9 (6)
P	C(2)	F(5)	115.8 (6)
P	C(2)	F(6)	114.5 (5)
F(4)	C(2)	F(5)	100.6 (8)
F(4)	C(2)	F(6)	108.2 (8)
F(5)	C(2)	F(6)	104.7 (8)
O(1)	C(3)	C(4)	114.2 (6)
O(1)	C(3)	C(5)	123.2 (7)
C(4)	C(3)	C(5)	122.7 (6)
C(3)	C(5)	C(6)	121.5 (6)
O(2)	C(6)	C(5)	122.5 (7)
O(2)	C(6)	C(7)	113.9 (6)
C(5)	C(6)	C(7)	123.5 (6)

... Table 2.5 Continued. Bond Angles^a for F(CF₃)₃P(acac) (4)

atom 1	atom 2	atom 3	angle
F(CF ₃) ₃ P(acac) (4)			
F(1)	P	O(1)	89.15 (5) ^b
F(1)	P	O(2)	89.10 (5)
F(1)	P	C(1)	174.70 (6)
F(1)	P	C(2)	91.96 (6)
F(1)	P	C(3)	86.84 (6)
O(1)	P	O(2)	92.06 (5)
O(1)	P	C(1)	85.55 (6)
O(1)	P	C(2)	175.33 (6)
O(1)	P	C(3)	89.72 (6)
O(2)	P	C(1)	90.98 (6)
O(2)	P	C(2)	83.43 (6)
O(2)	P	C(3)	175.55 (6)
C(1)	P	C(2)	93.32 (7)
C(1)	P	C(3)	93.23 (7)
C(2)	P	C(3)	94.87 (7)
P	O(1)	C(4)	125.8 (1)
P	O(2)	C(7)	125.5 (1)
P	C(1)	F(2)	112.2 (1)
P	C(1)	F(3)	113.8 (1)
P	C(1)	F(4)	111.6 (1)
F(2)	C(1)	F(3)	105.7 (1)
F(2)	C(1)	F(4)	106.6 (1)
F(3)	C(1)	F(4)	106.4 (1)
P	C(2)	F(5)	114.0 (1)
P	C(2)	F(6)	113.1 (1)
P	C(2)	F(7)	111.6 (1)
F(5)	C(2)	F(6)	105.7 (1)
F(5)	C(2)	F(7)	106.4 (1)
F(6)	C(2)	F(7)	105.5 (1)
P	C(3)	F(8)	113.8 (1)
P	C(3)	F(9)	114.6 (1)
P	C(3)	F(10)	110.5 (1)

... Table 2.5 Continued. Bond Angles^a for F(CF₃)₃P(acac) (4)

atom 1	atom 2	atom 3	angle
F(CF ₃) ₃ P(acac) (4)			
F(8)	C(3)	F(9)	106.2 (1) ^b
F(8)	C(3)	F(10)	105.8 (1)
F(9)	C(3)	F(10)	105.3 (1)
O(1)	C(4)	C(5)	113.9 (1)
O(1)	C(4)	C(6)	122.5 (1)
C(5)	C(4)	C(6)	123.6 (2)
C(4)	C(6)	C(7)	120.3 (2)
O(2)	C(7)	C(6)	122.5 (1)
O(2)	C(7)	C(8)	114.5 (1)
C(6)	C(7)	C(8)	123.0 (1)

^a In degrees.^b Numbers in parentheses are estimated standard deviations in the least significant digits.

earlier, the structure is well-defined. The acac moiety and the phosphorus and fluorine atoms in the "radial" girdle are essentially coplanar; the largest deviation from the least-squares plane defined by the acac ring, the phosphorus, and the two F atoms occurs for C(3) (-0.04(1) Å). The two axial CF₃ groups are almost exactly perpendicular to the radial plane, and the small bend of the C(1)-P-C(2) axis (178.8(4)°) tips the CF₃ groups very slightly toward the acac group. The present structure closely resembles that of F₄P(acac)² except that the P(acac) ring therein was found to have a pronounced boat shape.

A comparison of the structures of **3** and F₄P(acac)² with those of analogous six-coordinate carbamates^{16,17} shows that the larger P(acac) ring gives rise to an almost undistorted octahedral geometry (e.g. O(1)-P-O(2) = 95.4(2)°) at phosphorus, whereas the rather acute carbamate O-P-O bite angles of ca. 72° produce significant distortions from idealized octahedral geometry.^{16,17}

2.3.2 Structure of F(CF₃)₃P(acac) (**4**)

The six-coordinate geometry at phosphorus is also revealed in the structure of **4** (Figure 2.4). Metrical parameters are given in Tables 2.4 and 2.5. Notably, this is the first neutral λ⁶-phosphorane structure in which two CF₃ groups do not occupy mutually trans axial sites; instead all three are mutually cis, in a facial arrangement. The structure of **4** cannot be regarded as derived from **3** by simple replacement of a radial F by a CF₃ group.¹⁶ The second anomalous feature in this structure is the unusual folding of the acac ring about the O(1)-O(2) axis; as a result the plane defined by the acac ring atoms deviates by 27° from the plane defined by P, C(2), C(3), O(1), and O(2). It is significant also that the ring folds toward the unique axial fluorine atom. Both of these features appear to result from crowding within compound **4**.

Detailed comparison of **4** with F(CF₃)₃P(O₂CN(CH₃)₂)¹⁷ and CH₃(CF₃)₃-P(O₂CN(CH₃)₂),¹⁶ which have a meridional arrangement of CF₃ groups, shows the

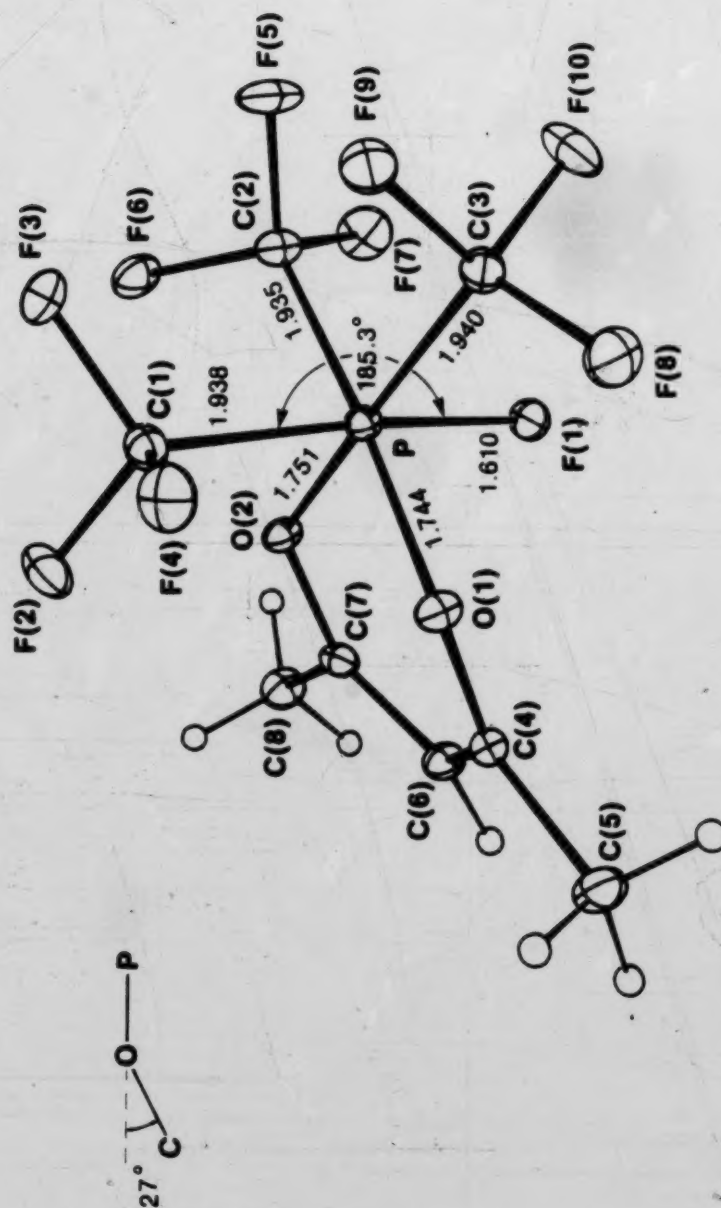


Figure 2.4 Perspective drawing of $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ (4) showing the numbering scheme. Thermal ellipsoids are shown at the 50% level except for hydrogens, which are drawn artificially small. Data collection courtesy of Dr. R.G. Ball, Structure Determination Laboratory, University of Alberta. Structure solution courtesy of Dr. M. Cowie.

carbamate structures to be almost superimposable. The orientations of the axial CF_3 groups of these carbamates (diagrammed in Figure 2.5) show that they are almost eclipsed to each other, and one fluorine atom on each of these CF_3 groups is almost eclipsed with O(2) of the carbamate chelate lying in the radial plane. Although this arrangement gives rise to slightly unfavorable nonbonded contacts between O(2) and these two proximal fluorines, the other two fluorines on these CF_3 groups adopt a favored, *staggered*, orientation with respect to the other three radial substituents. In addition, these three radial substituents (O(1), CH_3 , CF_3 or O(1), F, CF_3 on the respective carbamate compounds) are spread apart (angles at phosphorus are about 100°), further minimizing contacts of the radial substituents with fluorine atoms in the axial CF_3 groups. This relationship arises because of the small bite angle of the carbamate group and the relatively small angle (ca. 88°) between the radial CF_3 groups and the chelate. This orientation of the radial CF_3 group means that one C-F bond is eclipsed with the other radial group (F or CH_3), and this aspect has important implications regarding the differences between compound 4 and the carbamates.

Replacing the carbamate group by acac provides a ligand with a larger bite angle (95° vs 72°). As a result the projections of the F-C-F angles of two axial CF_3 groups (for the isomeric structure analogous to A in Figure 2.5) onto the O-P-O angle show greater interference, with presumably increased repulsive interactions between these moieties. In addition, less room is available for the spreading of the radial groups, so unfavorable contacts between the axial CF_3 groups and the radial substituents therefore become more severe. The influence of the radial CF_3 group becomes extremely important, since in order for it to remain staggered with respect to the axial groups, one of its C-F bonds must be eclipsed with one of the radial groups (as observed in the carbamate structures^{16,17}). The constricted radial plane makes this contact highly unfavorable, and the more favorable facial arrangement of structure 4 (shown in Figure 2.1) results. Furthermore, folding of the acac ligand bends this group away from the bulky CF_3 group towards the smaller F atom, creating additional space for the single axial CF_3 group. Finally, the axial CF_3 group bends

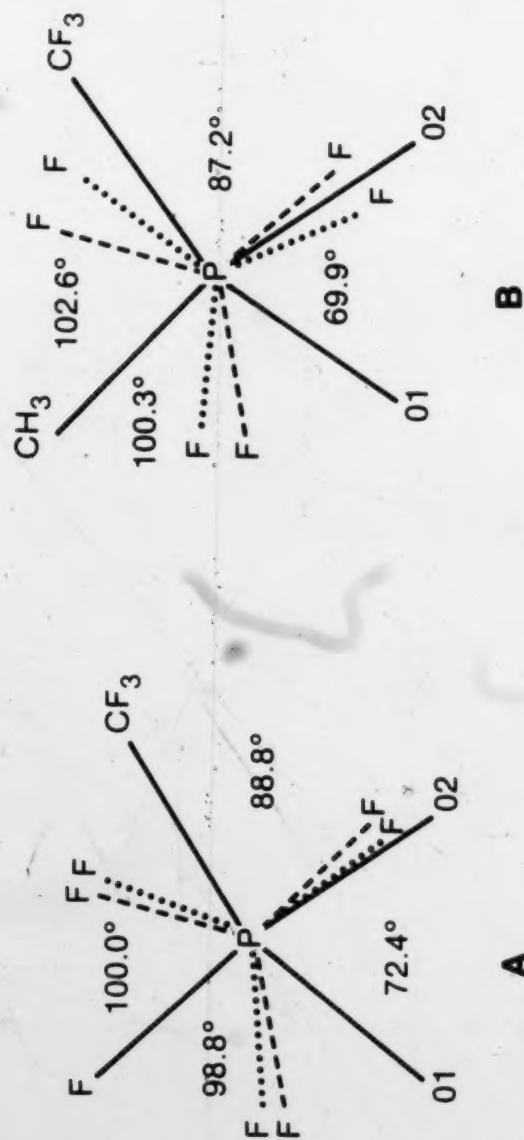


Figure 2.5 Projections of the axial CF_3 groups onto the radial planes in $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ (A) and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ (B). The dashed lines correspond to the C-F bonds above the radial plane, and the dotted lines correspond to the C-F bonds below this plane. The angles shown are those between adjacent radial substituents.

slightly toward the acac group, further reducing contacts with the two radial CF_3 groups. The resultant structure can be seen to provide minimal intramolecular interactions.

The acac group in **4** is essentially planar apart from a slight boat like bending of C(6) ($-0.143(2)$ Å from the plane). In spite of the folding of the acac group, all parameters within this ring resemble those in **3** and in $\text{F}_4\text{P}(\text{acac})$.² The O-P-O angles within these acac compounds are much larger than those displayed by the carbamates (ca. 72°). This ring strain in carbamates may account for the tendency of these compounds to display fluxionality through formation of λ^5 -phosphoranes with a monodentate ligand.

2.3.3 Comparison of Radial Bond Lengths in Hypervalent Phosphorus Compounds

Selected bond lengths of five formal (12-P-6) systems are given in Table 2.6. In the acetylacetonate series the P-F and P-O distances are somewhat longer in the CF_3 substituted compounds as compared to those in the fully fluorinated molecule (**1**). The lower electronegativity of CF_3 vs. F suggests that increasing CF_3 substitution decreases the Lewis acid strength of the phosphorus atom, resulting in a general weakening of the bonding. There appears to be no significant difference between the axial and radial P-F bonds in this series. The longer average radial P-F distance in **3** versus that in **1** parallels the longer P-O distances in **4** and can be attributed to the weaker acid strength of phosphorus in **4**. The P-O bond lengths in the carbamate derivatives average $1.81(4)$ Å¹⁸ in $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ and $1.85(7)$ Å in $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$; both are substantially longer than those in the acetylacetonate derivatives. Presumably this weaker bonding is due to the greater ring strain of the carbamate ligand. The only P-F distance available in the carbamate series is that for $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ in which the F atom is radially bound. This distance is a little shorter than the axial F in **4**, but it is difficult to attribute this difference to axial vs. radial location since the lengthening of the P-O bonds

Table 2.6 Bond Distances (Å) in Phosphorus(V) Acetylacetonates and Carbamates

	P-F		P-O		P-CF ₃		
	rad	ax			rad	ax	ref
F ₄ P(acac) ^a (1)	1.568 1.568	1.572 1.574 1.580 1.576 1.570 1.588	1.715 1.720 1.723 1.719		— —	— —	2
F ₂ (CF ₃) ₂ P(acac) (3)	1.615 (4) 1.594 (4)	1.745 (5)	1.741 (5) 1.745 (5)		— —	1.869 (8) 1.888 (8)	this work
F(CF ₃) ₃ P(acac) (4)	—	1.612 (1)	1.752 (1) 1.746 (1)		1.938 (2) 1.942 (2)	1.940 (1) —	this work
F(CF ₃) ₃ P(O ₂ CN(CH ₃) ₂)	1.590 (3)	—	1.832 (3) 1.778 (3)		1.904 (5) —	1.911 (5) 1.926 (6)	17
CH ₃ (CF ₃) ₃ P(O ₂ CN(CH ₃) ₂)	—	—	1.808 (5) 1.901 (5)		1.930 (9)	1.944 (9) 1.960 (9)	16

^a Standard deviations in the P-F and P-O bond lengths of F₄P(acac) are 0.002.

and the concomitant weakening of this interaction may also be responsible. There is also some variation in the P-C distances involving the CF_3 groups, and it appears that this variation is primarily steric in origin. In general the more crowded molecules show larger P- CF_3 distances. $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ displays shorter P-C distances than those in the more crowded $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ molecule (*vide supra*), whereas the P-C distances in $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ are very similar.

None of the structural differences between these molecular structures can be attributed to significant axial/ radial bonding differences, and this is further supported by the pattern of $^1\text{J}_{\text{PF}}$ values (*vide infra*).

2.3.4 The Properties of $\text{F}_4\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ (8)

The preparation and characterization of a series of neutral hexacoordinate (N, N-dimethylcarbamato-O,O')phosphorus(V) compounds with the general formula $\text{F}_{4-n}(\text{CF}_3)_n\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ ($n = 1-3$) and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ has been reported.^{16,17} To date, the preparation of the tetrafluoro analogue in this series has been elusive.

The solid white compound (8) is extremely moisture sensitive, becoming a clear colorless liquid when exposed to air. Because of this sensitivity, reliable mass spectroscopic data and elemental analysis could not be obtained. The compound was characterized by multinuclear NMR in solution.

The ^{31}P NMR spectrum of 8 indicates that $\text{F}_4\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ was prepared. The signal at -140.7 ppm was a pentet of broad lines (22° C) indicative of a fluxional system containing a hexacoordinate phosphorus center. This was expected, as some fluxional behaviour has been observed for all the analogous dimethylcarbamates ($\text{F}_{4-n}(\text{CF}_3)_n\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ ($n = 1-3$) and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$). Cooling the

NMR solution of **8** to -20°C stopped the fluorine exchange and the ^{31}P NMR spectrum became a triplet of triplets with $^1\text{J}_{\text{PF}}$ coupling constants of 838 and 842 Hz for axial and radial fluorines, respectively. The ^{19}F NMR spectrum shows the axial fluorines to resonate at a higher frequency [-58.4 ppm] than the radial fluorines [-80.6 ppm]. This assignment is based on observations of high-frequency shifts (-58.9 to -59.6 ppm) for axial fluorines seen in the other members of this dimethylcarbamate series.^{16,17}

2.3.5 Nuclear Magnetic Resonance Spectra

In contrast to the carbamates^{16,17} the compounds **1-7** are not fluxional, so all the parameters have been obtained from normal-temperature spectra. All patterns are consistent with the geometrical structures proposed, and all spectra are first order. Notably all of these compounds exhibit the high-field ^{31}P NMR chemical shifts characteristic of six-coordinate geometry. NMR spectral parameters are given in Table 2.7.

The simplest spectra are those shown by **3**. The high-field chemical shift of the directly bound fluorine is reminiscent of the trend shown by the carbamates^{16,17} and is in accord with the suggestion of Sheldrick et al.² that radial fluorines (i.e., the fluorine atoms that are coplanar with the chelate ligand) have the higher-field shifts. This assignment is strongly supported by the solid-state structure, but of course there is an implicit assumption that the solid-state and solution-state structures are the same. The spectrum could be equally well assigned if the high-field chemical shifts were not uniquely associated with radial positioning. Although this compound could be a fluxional mixture of axial and radial fluorine positions, it is unlikely in this system because the related molecules do not show any evidence for such behavior. The simplicity of the spectrum rules out a structure containing one axial and one radial fluorine, which would be second order.

Assuming that the solid-state structure **4** prevails in solution, the NMR spectral parameters can be easily assigned. The simple first-order ^{31}P NMR spectrum of **4**

Table 2.7 NMR Parameters for (acac), (aminoacac), and (methylaminoacac)phosphorus(V) Compounds (1-7)

	$^1\text{H}, ^c \delta$	$^{19}\text{F}, ^d \phi$	$^{31}\text{P}\{^1\text{H}\}, ^e \sigma$	coupling constants (Hz)		
				$^1\text{J}_{\text{PF}}$	$^2\text{J}_{\text{PF}}$	others
(Pentane-2,4-dionato)phosphorus(V) Compounds						
1^a	7.7 ^f	-69.0 ^g (2) ^h	-148.7 ⁱ	756.5 (rad) ^j	$^2\text{J}_{\text{FF}} = 58.5$	$^4\text{J}_{\text{PH}} = 2.0$
	3.9	-50.5 ^g (2)		819.0 (ax) ^j	$^2\text{J}_{\text{FF}} = 58.5$	
2A^b (major)	7.5	-79.7 ^k (1)	-151.7 ^k	883.9 (rad)	$^2\text{J}_{\text{FF}} = 53.8$	$^3\text{J}_{\text{FF}} = 13.1$
	3.4	-70.1 ^l (3)		143.4	$^3\text{J}_{\text{FF}} = 13.0$	$^3\text{J}_{\text{FF}} = 13.0$
		-59.1 ^m (2)		930.2 (ax)	$^2\text{J}_{\text{FF}} = 53.8$	$^3\text{J}_{\text{FF}} = 13.0$
2B^b (minor)	7.5	-75.3 ^m (2)	-151.0 ^k	896.5 (rad)	$^2\text{J}_{\text{FF}} = 61.3$	$^3\text{J}_{\text{FF}} = 14.4$
	3.5	-70.5 ^l (3)		147.8	$^3\text{J}_{\text{FF}} = 14.4$	$^3\text{J}_{\text{FF}} = 3.0$
		-64.4 ^k (1)		830.0 (ax)	$^2\text{J}_{\text{FF}} = 61.5$	$^3\text{J}_{\text{FF}} = 3.0$
3^b	7.7	-77.3 ⁿ (2)	-151.2 ^o	987.0 (rad)	$^3\text{J}_{\text{FF}} = 15.0$	
	4.0	-68.8 ^g (6)		163.4	$^3\text{J}_{\text{FF}} = 15.0$	
4^a	7.6	-64.0 ^p (1)	-158.4 ^q	890.6 (ax)	$^3\text{J}_{\text{FF}} = 7.6$	$^3\text{J}_{\text{FF}} = 13.8$
	3.8	-60.8 ^r (3)		94.0 (ax)	$^3\text{J}_{\text{FF}} = 7.6$	$^4\text{J}_{\text{FF}} = 9.9$
		-59.2 ^m (6)		95.3 (rad)	$^3\text{J}_{\text{FF}} = 13.8$	$^4\text{J}_{\text{FF}} = 9.9$
5^a	8.4 ^f	-60.3 ⁿ (3)	-147.8 ^s	—	$^2\text{J}_{\text{PH}} = 8.0$	$^4\text{J}_{\text{FF}} = 11.1, ^4\text{J}_{\text{PH}} = 2.0$
	7.8 ^f	-59.4 ^t (6)		63.9 (rad)	$^4\text{J}_{\text{FF}} = 11.1$	
	4.1			94.7 (ax)		

Table 2.7 continued on next page.

... Table 2.7 continued.

	$^1\text{H}, ^c \delta$	$^{19}\text{F}, ^d \phi$	$^{31}\text{P}(\text{}^1\text{H}), ^e \sigma$	coupling constants (Hz)		
				$^1\text{J}_{\text{PF}}$	$^2\text{J}_{\text{PF}}$	others
(4-aminopent-3-en-2-onato)phosphorus(V) Compounds						
6	7.86	-65.9 ⁿ (3)	-176.4 ^s	—	86 (rad)	$^4\text{J}_{\text{FF}} = 12.0$
	7.71	-65.6 ^t (6)			128 (ax)	$^2\text{J}_{\text{PH}} = 0$
	7.64					$^2\text{J}_{\text{PH(N)}} = 12.2$
	4.44					
	1.59					
7	8.36 ^f	-63.8 ⁿ (3)	-164.7 ^s	—	57.9 (rad)	$^4\text{J}_{\text{FF}} = 10.8$
	8.02	-61.9 ^t (6)			85.5 (ax)	$^2\text{J}_{\text{PH}} = 7.0$
	7.85					$^3\text{J}_{\text{PH}} = 5.6$
	6.77 ^f					
	4.58					

^a In CD_2Cl_2 .^b In CDCl_3 .^c Relative to Me_4Si .^d Relative to CFCl_3 (negative values indicate shift to high field of standard).^e Relative to 85% H_3PO_4 (negative values indicate shift to high field of standard).^f Doublet.^g Doublet of triplets.^h Relative intensity.ⁱ Triplet of triplets.^j Position of substituent: rad = coplanar with O atoms of acac substituent; ax = perpendicular to plane containing O atoms of acac.

... footnotes for Table 2.7 continued.

-
- k Doublet of triplet of quartets.
 - l Doublet of doublets of triplets.
 - m Doublet of doublets of quartets.
 - n Doublet of septets.
 - o Triplet of septets.
 - p Doublet of septets of quartets.
 - q Doublet of doublets (accidental degeneracy of $2J$ pf).
 - r Doublet of doublets of septets.
 - s Septet of quartets.
 - t Doublet of quartets.

(Figure 2.6) shows a low frequency signal at -158.4 ppm. The phosphorus signal is split into a doublet of decatets indicating strong $^1J_{\text{PF}}$ coupling to the lone fluorine and a smaller $^2J_{\text{PF}}$ coupling to nine CF_3 fluorines. The $^2J_{\text{PF}}$ coupling constants are similar enough, in 4, to give an apparent doublet of decatets instead of the expected doublet of quartets of septets, in the ^{31}P NMR spectrum. In addition, the unique fluorine has a relatively low ^{19}F chemical shift, -64.0 ppm, implying an axial position as is also indicated by the crystal structure. The two CF_3 environments are clearly distinguishable with an expected 2:1 relative intensity ratio (Figure 2.7). The chemical shift and coupling constant difference between the CF_3 types is small, but the relative intensity and coupling constant patterns indicate clearly that the axial CF_3 has the higher field shift and the smaller $^2J_{\text{PF}}$ value.

The NMR spectra of 2 clearly show that isomers 2A and 2B are both present, in 2:1 relative proportions. The assignment of the spectra is based on the association of high-field ^{19}F shifts with the radial directly bound fluorine atoms. The major isomer therefore has structure 2A with one radial F atom at -79.7 ppm, and the minor isomer has structure 2B with two radial F atoms at -75.3 ppm. The relative proportions of major/minor isomers is the reverse to that which exists for the carbamate analogue. It may be significant that for these acetylacetonates the major isomeric component of the system $\text{F}_3(\text{CF}_3)\text{P}(\text{acac})$ is the isomer with two axial F atoms and the only form of $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ is that with an axial F. In contrast, the only isomer of $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ found is that with a radial F atom and the major isomer of $\text{F}_3(\text{CF}_3)\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ is apparently that with two radial F atoms. The pattern suggests that acetylacetonate derivatives prefer axial substitution and carbamates prefer radial substitution of fluorine, possibly the ultimate effect of the crowding discussed above. As a result the behavior of the $\text{F}_2(\text{CF}_3)_2\text{PL}$ systems ($\text{L} = \text{O}_2\text{CN}(\text{CH}_3)_2$ or acac) seems to be anomalous in apparently having the same structure for both ligands; however, it should be recalled from the structural discussion that this substitution pattern is consistent with steric arguments, with the bulkier CF_3 groups

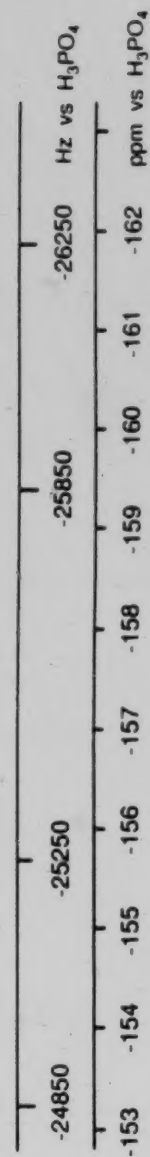
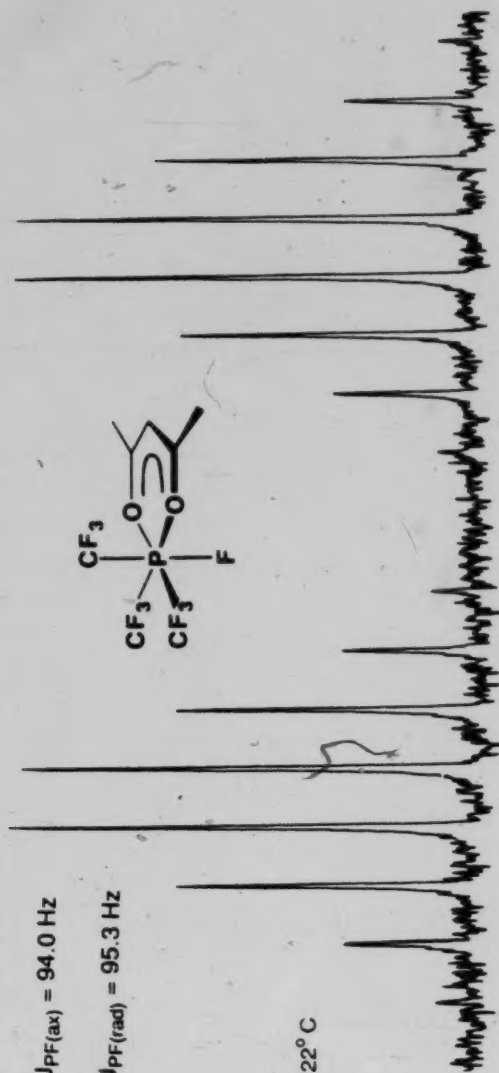
^{31}P NMR (161.98 MHz)

$^1J_{\text{PF}} = 890.6 \text{ Hz}$

$^2J_{\text{PF(ax)}} = 94.0 \text{ Hz}$

$^2J_{\text{PF(rad)}} = 95.3 \text{ Hz}$

22°C

Figure 2.6 The ^{31}P NMR spectrum of $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ (4). Courtesy of Dr. N. Burford.

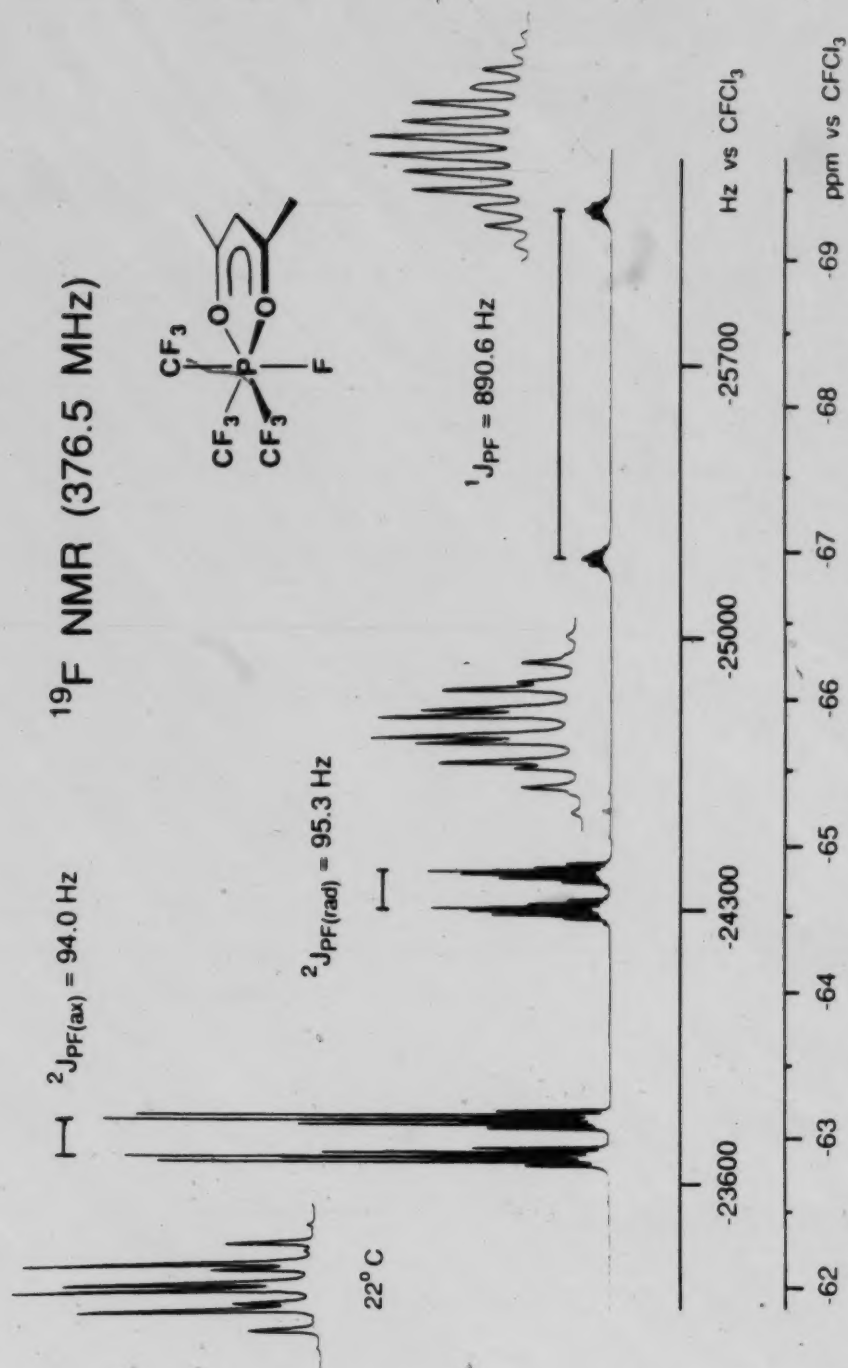


Figure 2.7 The ^{19}F NMR spectrum of $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ (4). Courtesy of Dr. N. Burford.

occupying the sterically favored positions, which can be but are not necessarily the same in the carbamate and acac species (*vide supra*).

Another notable feature of the CF_3 portion of the spectra of 2-4 is the lack of contrast between radial and axial $^2J_{\text{PF}}$ values and the corresponding ^{19}F chemical shifts. In contrast $^2J_{\text{PF}}$ values for radial CF_3 in the carbamate¹⁷ groups were apparently significantly smaller than axial values.

The existence of two CF_3 environments in 5 is clearly visible in the shift and coupling constant patterns, and the spectra also show the appropriate 2:1 relative intensity ratio expected for either possible static structure. This is the only acac derivative that is seen to display demonstrably different axial/ radial $^2J_{\text{PF}}$ values for its CF_3 groups. Structure 5 may be the most probable isomeric form on the basis of associating the large value of $^2J_{\text{PF}}$ (with a total relative intensity of 2 units) with the axial CF_3 groups in parallel to the behavior of the carbamates.¹⁷

In general *cis* $^3J_{\text{FF}}$ values are in the range of 15 Hz whereas *trans* values are significantly smaller in parallel to the case of carbamates.¹⁷ In 4 $^3J_{\text{FF}}(\text{trans})$ is half the value of $^3J_{\text{FF}}(\text{cis})$ while in 2B the effect is more pronounced and the *trans* value is 3.0 Hz.

Directly bound fluorines in both acac and carbamate systems, which have high-field NMR chemical shifts, show a generally consistent trend for *major* isomers: $^1J_{\text{PF}}(\text{axial})$ is larger than $^1J_{\text{PF}}(\text{radial})$. Also, in both systems the minor isomers violate this trend: $^1J_{\text{PF}}(\text{radial}) \geq ^1J_{\text{PF}}(\text{axial})$.

The ^1H NMR spectra (Table 2.7) of all of the (pentane-2,4-dionato)phosphorus(V) compounds show two signals associated with the chelate, with a 6:1 integration ratio. The larger signal corresponds to the equivalent methyl groups, and in two cases this is split by weak coupling to the phosphorus. In the asymmetric frameworks these methyl groups do not show asymmetry. The unique proton is responsible for the other signal. This proton shows no coupling characteristics, contrary to the first NMR reports^{1,2} for 1.

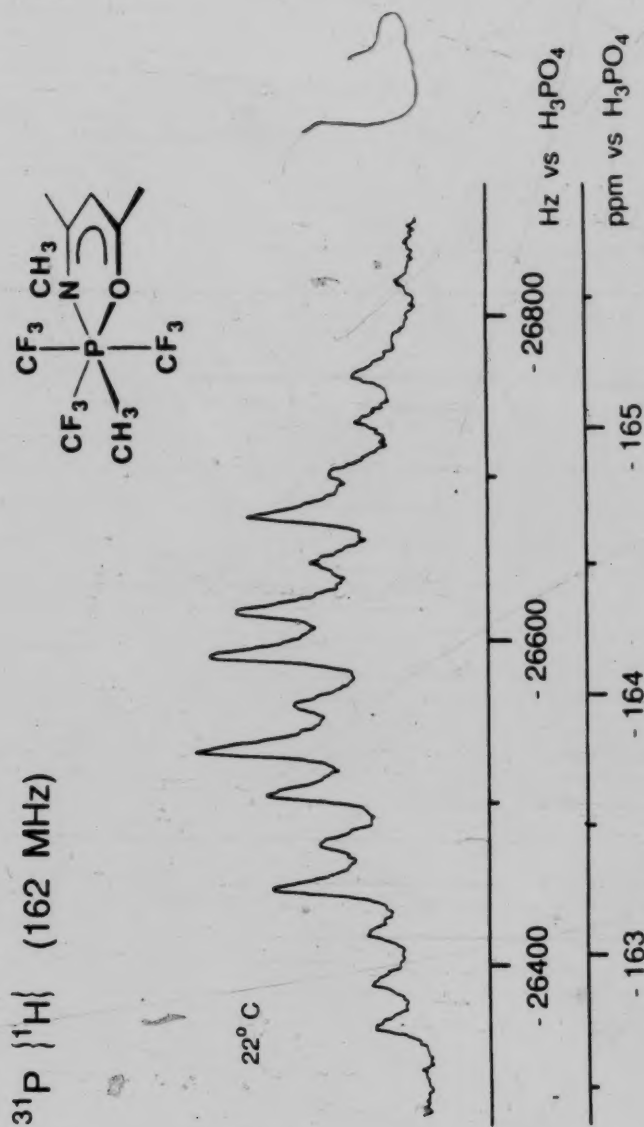


Figure 2.8 The ^{31}P NMR proton decoupled spectrum of $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{methylaminoacac})$ (7).

Although **6** and **7** could not be isolated for analysis, their structures are readily deduced from solution NMR spectra. The ^{31}P NMR spectrum of **7** (Figure 2.8) is a septet of quartets at -164.7 ppm, indicating two CF_3 environments in a 2:1 ratio. The lack of sharpness of the ^{31}P signal of **7** suggests possible quadrupolar broadening by the bonding nitrogen from the ligand. The ^{19}F NMR spectrum of **7** (Figure 2.9) confirms that the CF_3 groups are in a 2:1 ratio and the $^2J_{\text{PF}}$ coupling information suggests the two equivalent CF_3 groups are in the axial position similar to the structure of **5**. In addition, if two CF_3 groups were in radial positions one would expect three signals in the ^{19}F NMR, because of the unsymmetrical nature of the chelating ligand. From this NMR data one can assign compound **7** the structure shown in Figure 2.1.

Using similar arguments **6** can also be shown to have a structure analogous to **7**. The ^{19}F NMR spectrum of **6** (Figure 2.10) shows two overlapping fluorine signals in a 2:1 ratio. The ^{31}P NMR spectrum of **6** (Figure 2.11) shows a low frequency signal at -176.4 ppm. The large coupling pattern is a septet of quartets similar to **5** and **7**. Surprisingly, the fine structure shown in the undecoupled ^{31}P NMR spectrum of **6** (Figure 2.11) shows only $^2J_{\text{PH}}$ coupling to the amino proton, with no apparent $^2J_{\text{PH}}$ coupling to the methyl group on phosphorus. The ^1H NMR spectrum of **6** has a signal with the expected integration and chemical shift of a methyl group attached to phosphorus confirming its existence, but again no $^2J_{\text{PH}}$ coupling is observed. It appears that the geminal P-H coupling in **6** is zero ($^2J_{\text{PH}} = 0$).

Although geminal phosphorus-proton ($^2J_{\text{PH}}$) coupling has not been thoroughly investigated, there have been several studies of the structural implications of geminal proton-proton ($^2J_{\text{HH}}$) coupling.¹⁹ There is no satisfactory theory that can predict the magnitude and sign of these coupling constants, however, several empirical trends have been established. These trends have been discussed elsewhere²⁰ and are summarized as follows:

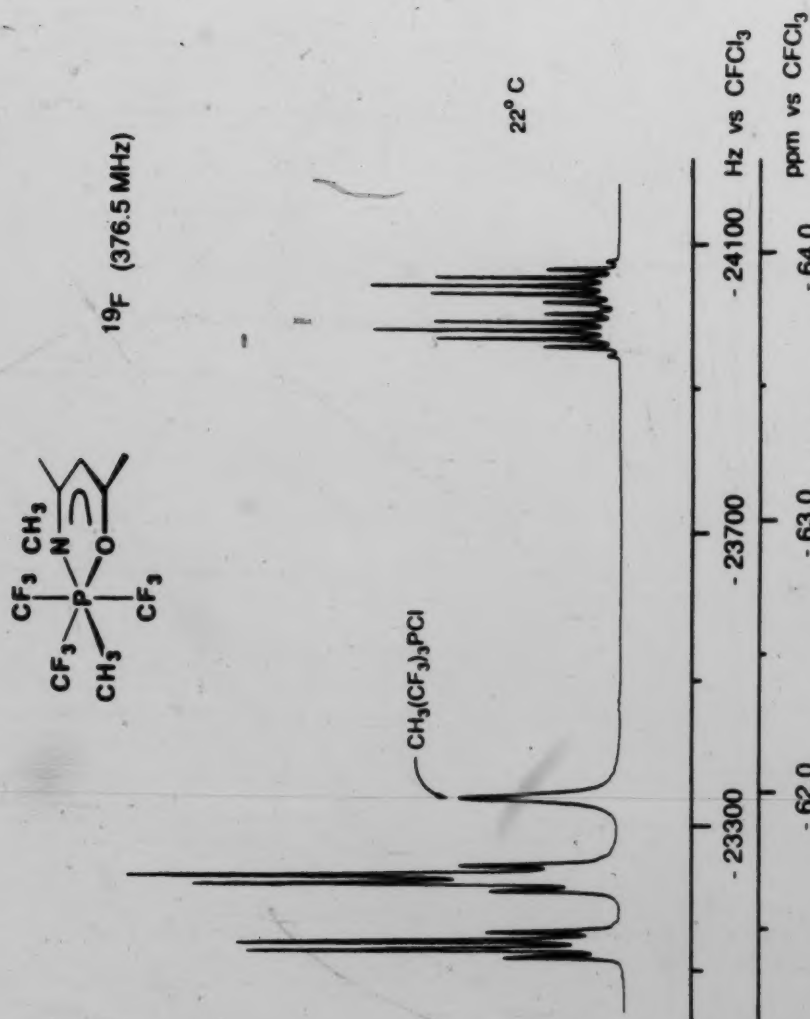
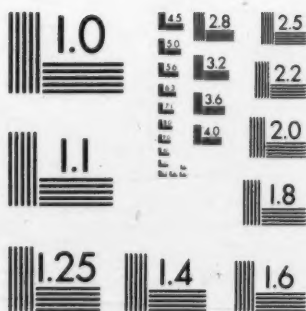


Figure 2.9 The ^{19}F NMR spectrum of $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{methylaminoacac})$ (7).

2



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STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

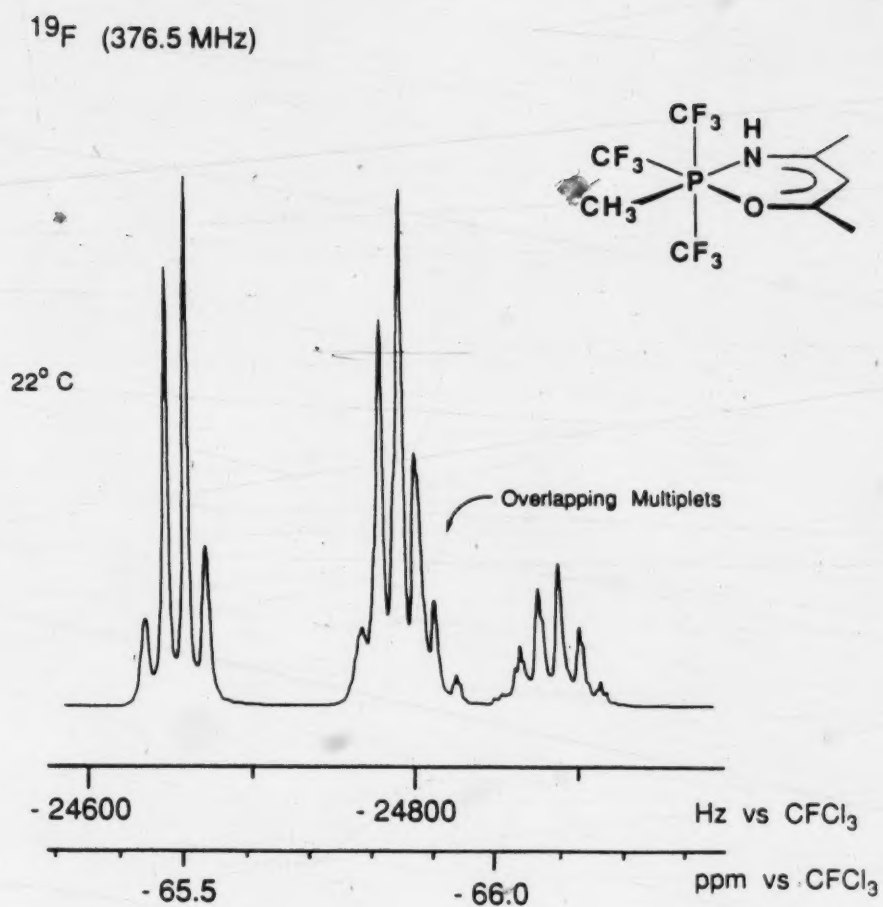


Figure 2.10 The ^{19}F NMR spectrum of $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{aminoacac})$ (6).

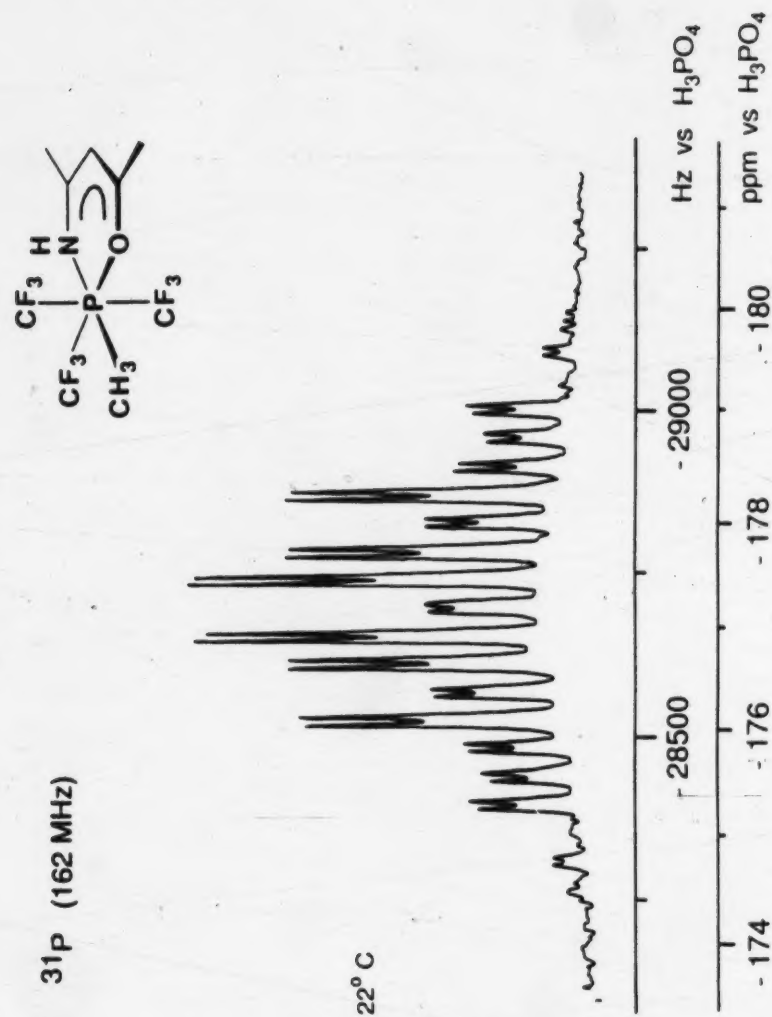


Figure 2.11 The ^{31}P NMR spectrum of $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{aminoacac})$ (6).

- (1) as the carbon becomes more *s*-like in its hybridization the $^2J_{HH}$ coupling becomes more positive;
- (2) as electronegative groups are substituted at the α position the $^2J_{HH}$ coupling becomes more positive;
- (3) as electronegative groups are substituted at the β position the $^2J_{HH}$ coupling becomes more negative; and
- (4) the presence of a π -electron system next to the CH_2 group leads to a negative shift of $^2J_{HH}$.

These trends should also apply to geminal phosphorus-proton couplings, since phosphorus is also a spin one-half nucleus with a natural abundance of ~100%.

The $^2J_{PH}$ coupling in the five-coordinate phosphorus precursors of compounds 5-7 are 12.0 Hz and 13.6 Hz for $CH_3(CF_3)_3PCl$ and $CH_3(CF_3)_3PF$, respectively. Compounds 5-7 are analogous $[CH_3(CF_3)_3P]$ λ^6 -phosphoranes with differing bidentate chelating ligands. The chelating ligands are acac, (methylamino)acac, and aminoacac for compounds 5, 7, and 6, respectively. One can observe a decrease in the $^2J_{PH}$ coupling constants when comparing compounds 5 (8.0 Hz, O), 7 (7.0 Hz, N(Me)), and 6 (0 Hz, N(H)). The magnitude of the $^2J_{PH}$ coupling is strongly affected by the nature of the chelating ligand, which in each case is a delocalized π -electron system.

2.4 Conclusion

This chapter presented a series of related neutral hexacoordinate compounds (1-8) containing a six-membered chelating ring. Their structure and unusual NMR spectral properties have been examined. These derivatives all possess a characteristic low-

frequency chemical shift in their ^{31}P NMR spectra and all display clean first order NMR spectra.

Although the solid-state structure of $\text{F}_2(\text{CF}_3)_2\text{P}(\text{acac})$ (3) possessed a similar geometry to analogous λ^6 -phosphorus compounds, the structure of $\text{F}(\text{CF}_3)_3\text{P}(\text{acac})$ (4) unexpectedly suggests that the lone fluorine on phosphorus occupied the axial position, in preference to the more bulky CF_3 groups which usually occupy the more open axial sites. In addition, the plane formed by the acac ring was bent towards this axial fluorine (Figure 2.3). Detailed analysis of the intermolecular interactions, which would arise in the different isomeric structures, show that these features are due simply to steric effects within the molecule.

Finally, the use of unsymmetrical ligands to prepare $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{aminoacac})$ (6) and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{methyldaminoacac})$ (7) leads to straightforward structural assignments from multinuclear NMR spectroscopy.

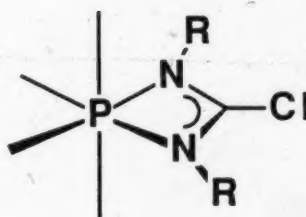
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- 2 Sheldrick, W.S.; Hewson, M.J.C., *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, 1978, **33B**, 834.
- 3 Burford, N.; Kennepohl, D.; Cowie, M.; Ball, R.G.; Cavell, R.G., *Inorg. Chem.*, 1987, **26**, 650.
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- 6 Lacey, M.J., *Aust. J. Chem.*, 1970, **23**, 841.
- 7 Data collection of **3** and **4** and structure solution of **3** courtesy of Dr. R.G. Ball, Structure Determination Laboratory, Department of Chemistry, University of Alberta. Structure solution of **4** courtesy of Dr. M. Cowie and the author, Department of Chemistry, University of Alberta. Ref. Nos. SR: 030122-04-85 and CAV 0285.
- 8 The X-ray crystallographic study for this molecule comprises report number SR:030122-04-85 from the Structure Determination Laboratory, Department of Chemistry, University of Alberta.
- 9 The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions.
- 10 *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I.
- 11 The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by B. A. Frenz (*Computing in Crystallography*; Delft University Press: Delft, Holland, 1978: pp 64-71) and several locally written or modified programs.
- 12 Main, P.; Lessinger, L.; Woofson, M.M.; Germain, G.; Declercq, J. P. *MULTAN 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York, York, England, and University of Louvain, Louvain, Belgium, 1982.
- 13 *International Tables for X-ray Crystallography*; Kynock: Birmingham, England, 1974; Vol. IV, Table 2.2B.
- 14 Reference 13, Table 2.3.1.

- 15 $\text{CH}_3(\text{CF}_3)_3\text{PF}$ also reacted with sodium acetylacetonate but gave an alternative product. This reaction is still under investigation.
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- 18 The esd quoted for an average value is the larger of either the standard deviation of the mean or an individual measurement.
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CHAPTER III

CARBODIIMIDE DERIVATIVES OF HEXACOORDINATE PHOSPHORUS(V)



3.1 Introduction

In this chapter a series of neutral compounds containing hexacoordinate phosphorus centers of the general formula $\text{Cl}_{4-n}(\text{CF}_3)_n \overline{\text{PN}(\text{R})\text{C}(\text{Cl})\text{NR}}$ ($n = 0-3$ and $\text{R} = \text{cyclohexyl}$ or isopropyl) (1-8), as shown in Figure 3.1, are described. These compounds are prepared by an apparent carbodiimide insertion into a P-Cl bond of a pentacoordinate phosphorus to form a four-membered chelating ring. The preparation of these compounds and their characterization by X-ray crystallography and by multinuclear NMR, infrared and mass spectroscopies are reported.

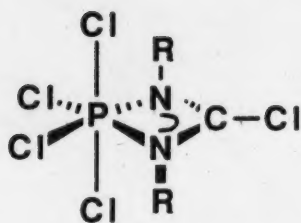
In addition, the chemical reactivity of these λ^6 -phosphoranes is discussed, including a nucleophilic substitution study based on compound 2. This is the first time the general chemistry of neutral hexacoordinate phosphorus compounds has been investigated. Two derivatives of 2, a phenylated derivative, $\text{Cl}_4 \overline{\text{PN}(\text{Pr}^i)\text{C}(\text{Ph})\text{NPr}^i}$ (9), and a hydrolysis product, $\text{Cl}_2(\text{O})\text{P}-\text{N}(\text{Pr}^i)\text{C}(\text{Cl})=\text{NPr}^i$ (10), are also reported.

Finally, two related neutral hexacoordinate phosphorus compounds (11 and 12) of the formula $\text{X}_4 \overline{\text{PN}(\text{Ph})\text{C}(\text{Ph})\text{NPh}}$ ($\text{X} = \text{Cl}, \text{F}$) were prepared from PX_5 and N,N -diphenylbenzamidine. The preparation and characterization by ^{31}P and ^1H NMR spectroscopies of 11 and 12 are reported.

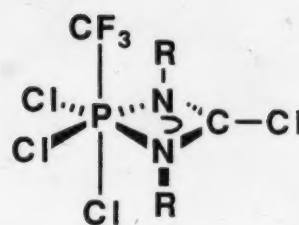
3.2 Experimental

3.2.1 General Procedures

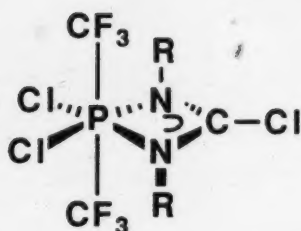
The trifluoromethyl phosphoranes CF_3PCl_4 , $(\text{CF}_3)_2\text{PCl}_3$, $(\text{CF}_3)_3\text{PCl}_2$ and $(\text{CF}_3)_3\text{CH}_3\text{PCl}$ were prepared according to published methods.¹ The reactants PCl_5 ,



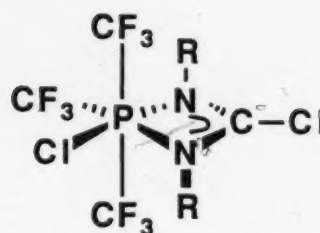
1, 2



3, 4

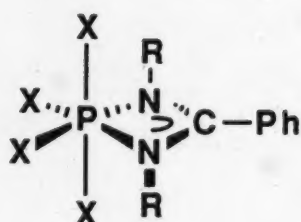


5, 6



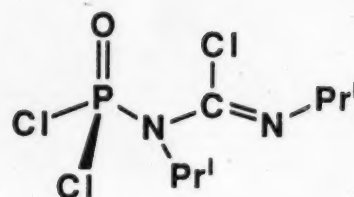
7, 8

R = cyclohexyl or isopropyl

9 R = Prⁱ

11 R = Ph, X = Cl

12 R = Ph, X = F



10

Figure 3.1 (Carbodiimide)phosphoranes (1-8, 10)
and (Benzamidine)phosphoranes (9, 11, 12).

dicyclohexylcarbodiimide (DCC) and diisopropylcarbodiimide (DPC) were obtained from Aldrich and used without further purification. Solvents were dried and distilled before use. The ^1H , ^{19}F , and ^{31}P spectra were obtained using Bruker WP200, WP400 and WP80 spectrometers. Samples recorded were CDCl_3 solutions (approximately 10% compound) in vacuum sealed 5mm NMR tubes. Mass spectra were recorded with an AEI MS-12 spectrometer operating at an ionizing voltage of 70 eV. Infrared spectra were recorded with a Polaris FTIR spectrometer using a 0.1 mm KBr solvent cell. All manipulations were carried out either on a high vacuum line or in a glove bag under dry argon.

3.2.2 Preparation of tetrachloro(N,N'-dicyclohexylchlorodiimido)phosphorus(V) (1)

A sample of PCl_5 (0.509 g; 2.44 mmol) was dissolved in CCl_4 (50 mL) under Ar in a round bottomed flask. To this stirred solution DCC (0.499 g; 2.42 mmol) was slowly added. The mixture was refluxed under Ar for 3 hours and then cooled to room temperature. The solvent was removed in vacuum to leave a white solid (mp 160 - 163° C).

Anal. for $\text{C}_{13}\text{H}_{22}\text{Cl}_5\text{N}_2\text{P}$:

Calcd.: C, 37.66; H, 5.35; Cl, 42.76; N, 6.76.

Found: C, 37.68; H, 5.26; Cl, 42.64; N, 6.78 %.

MS: m/e (Rel. int., % of strongest peak) identity : 378 (2.3) M - Cl; 242 (15.2) $\text{ClCN}_2\text{C}_{12}\text{H}_{22}$; 173 (7.6) PCl_4 ; 159 (21.9) $\text{ClCN}_2\text{C}_6\text{H}_{11}$; 101 (9.4) PCl_2 ; 83 (41.9) C_6H_{11} ; 67 (24.9) C_5H_7 ; 55 (100) C_4H_7 ; 41 (91.9) NCN .

3.2.3 Preparation of tetrachloro(N,N'-diisopropylchlorodiimido)phosphorus(V) (2)

A sample of PCl_5 (1.4717 g; 7.06 mmol) was dissolved in CCl_4 (60 mL) under Ar in a round bottomed flask. To this stirred solution DPC (1.1 mL; 7.03 mmol) was slowly

added by syringe. The mixture was refluxed under Ar for 3 hours and then cooled to room temperature. The solvent was removed in vacuum to leave a white solid (mp 76 - 78° C).

Anal. for $C_7H_{14}Cl_5N_2P$:

Calcd.: C, 25.14; H, 4.22; Cl, 53.00; N, 8.38.

Found: C, 25.75; H, 4.31; Cl, 50.94; N, 8.59 %.

MS : m/e (Rel. int., % of strongest peak) identity: 299 (23.2) M - Cl; 173 (64.5) PCl_4 ; 126 (11.1) $CN_2C_6H_{14}$; 104 (43.9) $ClCN_2C_2H_4$; 83 (12.5) $CN_2C_3H_7$; 69 (100) CNC_3H_7 ; 43 (90.3) C_3H_7 .

3.2.4 Preparation of trichloro(N,N'-dicyclohexylchlorodiimido)trifluoromethylphosphorus(V) (3)

A sample of DCC (0.180 g; 0.874 mmol) was weighed out into a glass reaction vessel. Then CCl_4 (5 mL) was distilled in followed by CF_3PCl_4 (0.2165 g; 0.895 mmol). The vessel was sealed under vacuum and allowed to warm to room temperature. The bottom end of the vessel was placed in an oil bath and warmed to 100° C for 3 hours to establish reflux. After cooling to room temperature the solvent was removed in vacuum to leave a white solid (mp 163 - 165° C).

Anal. for $C_{14}H_{22}Cl_4F_3N_2P$:

Calcd.: C, 37.52; H, 4.95; Cl, 31.64; N, 6.25.

Found: C, 38.74; H, 5.07; Cl, 28.42; N, 6.68 %.

MS : m/e (Rel. int., % of strongest peak) identity: 411 (20.8) M - Cl; 379 (1.6) M - CF_3 ; 206 (84.8) CF_3PCl_3 ; 177 (35.6) $CN_2C_{10}H_{17}$; 151 (19.7) $CN_2C_8H_{15}$; 124 (100) $CN_2C_6H_{11}$; 101 (22.2) Cl_2P ; 96 (20.9) NC_6H_{11} ; 83 (82.2) C_6H_{11} ; 69 (18) CF_3 ; 55 (15.2) C_4H_7 ; 41 (82.2) CN_2 .

3.2.5 Preparation of trichloro(N,N'-diisopropylchlorodiimido)trifluoromethyl-phosphorus(V) (4)

A sample of DPC (170 μ L; 1.09 mmol) was transferred by a syringe into a glass reaction vessel, attached to a vacuum line, and degassed three times via a freeze-thaw cycle. Then CCl_4 (4 mL) was distilled in, followed by CF_3PCl_4 (0.2630 g; 1.09 mmol). The vessel was sealed under vacuum and allowed to come to room temperature. The bottom end of the vessel was then placed in an oil bath and warmed to 100° C for 3 hours to establish reflux. After cooling to room temperature the solvent was removed in vacuum to leave a white solid (mp 73 - 75° C).

Anal. for $\text{C}_8\text{H}_{14}\text{Cl}_4\text{F}_3\text{N}_2\text{P}$:

Calcd.: C, 26.11; H, 3.83; Cl, 38.54; N, 7.61.

Found: C, 26.01; H, 3.66; Cl, 38.59; N, 7.51 %.

MS : m/e (Rel. int., % of strongest peak) identity: 333 (57.6) M - Cl; 299 (5.6) M - CF_3 ; 207 (84.2) Cl_3PCF_3 ; 173 (18.0) Cl_2PCF_3 ; 126 (40.3) $\text{CN}_2\text{C}_6\text{H}_{14}$; 111 (56.3) $\text{CN}_2\text{C}_5\text{H}_{11}$; 104 (19.2) Cl_2P ; 69 (100) CF_3 ; 43 (19.7) C_3H_7 .

3.2.6 Preparation of dichloro(N,N'-dicyclohexylchlorodiimido)bis-(trifluoromethyl)-phosphorus(V) (5)

A sample of DCC (0.60 g; 2.91 mmol) was weighed into a glass reaction vessel. Then CCl_4 (6 mL) was distilled in followed by $(\text{CF}_3)_2\text{PCl}_3$ (0.8113 g; 2.94 mmol). The vessel was sealed under vacuum and allowed to warm to room temperature. The bottom end of the vessel was placed in an oil bath and warmed to 100° C for 3 hours to establish reflux. After cooling to room temperature the solvent was removed in vacuum to leave a white solid (mp 154 - 157° C).

Anal. for $C_{15}H_{22}Cl_3F_6N_2P$:

Calcd.: C, 37.40; H, 4.60; Cl, 22.08; N, 5.81.

Found: C, 37.34; H, 4.68; Cl, 21.72; N, 5.88 %.

MS: m/e (Rel. int., % of strongest peak) identity: 445 (1.0) M - Cl; 411 (5.5) M - Cl₂; 241 (9.6) ClCN₂C₁₂H₂₂; 205 (45.8) F₆C₂ClP; 163 (15.8) CN₂C₉H₁₅; 124 (17.9) CN₂C₆H₁₁; 101 (12.2) Cl₂P; 83 (63.6) C₆H₁₁; 69 (61.8) CF₃; 55 (100) C₄H₇; 41 (79.6) CN₂.

3.2.7 Preparation of dichloro(N,N'-diisopropylchlorodiimido)bis(trifluoromethyl)-phosphorus(V) (6)

A sample of DPC (70 μ L; 0.45 mmol) was transferred by a syringe into a glass reaction vessel and attached to a vacuum line. It was degassed three times via a freeze-thaw cycle. Then CCl₄ (6 mL) was distilled in followed by (CF₃)₂PCl₃ (0.123 g; 0.446 mmol). The vessel was sealed under vacuum and allowed to warm to room temperature. The bottom end of the vessel was then placed in an oil bath and warmed to 100° C for 3 hours to establish reflux. After cooling to room temperature the solvent was removed in vacuum to leave a white solid (mp 114 - 117° C).

Anal. for $C_9H_{14}Cl_3F_6N_2P$:

Calcd.: C, 26.92; H, 3.15; Cl, 26.49; N, 6.98.

Found: C, 26.70; H, 3.37; Cl, 26.24; N, 6.79 %.

MS: m/e (Rel. int., % of strongest peak) identity: 365 (20.8) M - Cl; 331 (85.2) M - CF₃; 239 (40.7) C₂F₉Cl₂P; 205 (100) CF₃Cl₃P; 126 (39.5) CN₂C₆H₁₄; 111 (57.2) CN₂C₅H₁₁; 69 (80.6) CF₃; 43 (21.6) C₃H₇.

3.2.8 Preparation of chloro(N,N'-dicyclohexylchlorodiimido)tris(trifluoromethyl)-phosphorus(V) (7)

A sample of DCC (0.468 g; 2.27 mmol) was weighed into a glass reaction vessel. Then CCl₄ (6 mL) was distilled in followed by (CF₃)₃PCl₂ (0.848 g; 2.74 mmol). The vessel was sealed under vacuum and allowed to warm to room temperature. The bottom end of the vessel was placed in an oil bath and warmed to 100° C for 3 hours to establish reflux. After cooling to room temperature the solvent was removed in vacuum to leave a white solid (mp 148 - 150° C).

Anal. for C₁₆H₂₂Cl₂F₉N₂P:

Calcd.: C, 37.30; H, 4.30; Cl, 13.76; N, 5.44.

Found: C, 37.86; H, 4.35; Cl, 14.26; N, 5.62 %.

MS: m/e (Rel. int., % of strongest peak) identity: 479 (4.9) M - Cl; 445 (26.4) C₂F₆Cl₂PCN₂C₁₂H₂₂; 363 (31.5) C₃F₉ClCN₂C₆H₁₁; 327 (39.2) C₂F₆ClCN₂-C₆H₁₁; 273 (31.5) C₃F₉ClP; 239 (95.1) C₂F₆Cl₂P; 124 (13.3) CN₂C₆H₁₁; 83 (66.0) C₆H₁₁; 69 (77.5) CF₃; 55 (100) C₄H₇; 41 (72.5) CN₂.

3.2.9 Preparation of chloro(N,N'-diisopropylchlorodiimido)tris(trifluoromethyl)-phosphorus(V) (8)

A sample of DPC (430 µL; 2.75 mmol) was transferred by a syringe into a glass reaction vessel and attached to a vacuum line. It was degassed three times via a freeze-thaw cycle. Then CCl₄ (6 mL) was distilled in followed by (CF₃)₃PCl₂ (0.8760 g; 2.83 mmol). The vessel was sealed under vacuum and allowed to warm to room temperature. The bottom end of the vessel was then placed in an oil bath and warmed to 100° C for 3 hours to establish reflux. After cooling to room temperature the solvent was removed in vacuum to leave a white solid (mp 100 - 102° C).

Anal. for $C_{10}H_{14}Cl_2F_9N_2P$:

Calcd.: C, 27.61; H, 3.24; Cl, 16.30; N, 6.44.

Found: C, 27.65; H, 3.25; Cl, 16.31; N, 6.46 %.

MS: m/e (Rel. int., % of strongest peak) identity: 399 (14.0) M - Cl; 365 (14.9) M - Cl₂; 273 (51.4) C₃F₉ClP; 239 (80.4) C₃F₉P; 126 (3.3) CN₂C₆H₁₄; 111 (15.1) CN₂C₅H₁₁; 69 (100) CF₃; 43 (76.9) C₃H₇.

3.2.10 Preparation of tetrachloro(N,N'-diisopropylphenyl)diimido)-phosphorus(V) (9)

A sample of **2** (1.17 g, 3.49 mmol) was weighed into a round bottom flask and dissolved in diethyl ether. The solution was cooled to -78° C in a dry ice/acetone bath. A solution of phenyllithium (1.65 M, 2.22 mL, 3.58 mmol) was added dropwise over a period of one hour. The reaction mixture was allowed to warm to room temperature for three hours. A white precipitate (LiCl) formed and was allowed to settle. The solution was transferred by syringe to another flask and the solvent was removed under vacuum, leaving a pale yellow solid (mp 82 - 84° C).

Anal. for $C_{13}H_{19}Cl_4N_2P$:

Calcd.: C, 41.52; H, 5.09; Cl, 37.71; N, 7.45.

Found: C, 41.81; H, 5.92; Cl, 34.94; N, 6.70 %.

MS: m/e (Rel. int., % of strongest peak) identity: 305 (0.8) M - 2Cl; 262 (1.2) Cl₂PNCC₆H₅NC₃H₇; 235 (20.2) M - 4Cl; 219 (1.8) Cl₂PNCC₆H₅N; 203 (2.6) C₃H₇NCC₆H₅NC₃H₇; 126 (14.5) C₃H₇NCNC₃H₇; 111 (29.6) C₃H₇NCNC₂CH₄; 83 (22.7) C₃H₇NCN; 69 (100) C₃H₇NC; 43 (45.1) C₃H₇.

3.2.11 Preparation of (N,N'-diisopropylchlorodiiimido)phosphonicdichloride (10)

A sample of **2** (1.26 g, 3.77 mmol) was placed in a reaction vessel and dissolved in CCl₄. A sample of H₂O (0.069 g, 3.8 mmol) was added and the mixture stirred for two hours at room temperature. The CCl₄ was removed under vacuum, leaving a thick yellow liquid (bp 102° C, 0.5 mmHg).

Anal. for C₇H₁₄Cl₃N₂OP:

Calcd.: C, 30.08; H, 5.01; Cl, 38.05; N, 10.02.

Found: C, 28.65; H, 5.03; Cl, 38.46; N, 9.77 %.

MS: m/e (Rel. int., % of strongest peak) identity: 280 (0.2) M; 236 (0.2) M - C₃H₇; 152 (5.7) ClPOC₃H₇NC; 144 (4.6) Cl₂PONCN; 126 (22.4) C₃H₇CNCC₃H₇; 111 (36.5) C₃H₇NCNC₂H₄; 83 (10.2) C₃H₇NCN; 69 (100) C₃H₇NC.

3.2.12 Preparation of tetrachloro (N,N-diphenylbenzamidino)phosphorus(V) (11)

A sample of PCl₅ (1.11 g, 5.32 mmol) was weighed into a round bottom flask and dissolved in CCl₄ (200 ml). Then a sample of N,N-diphenylbenzamidine (1.45 g, 5.33 mmol), which was prepared by a literature method,² was added to the solution. The mixture was refluxed for 4 hours, cooled to room temperature, and the solvent was removed under vacuum, to leave a white solid (mp 238-242° C).

Anal. for C₁₉H₁₅Cl₄N₂P:

Calcd.: C, 51.32; H, 3.49; Cl, 31.91; N, 6.38.

Found: C, 53.22; H, 3.64; Cl, 30.35; N, 6.43 %.

MS: m/e (Rel. int., % of strongest peak) identity: 407 (3.9) M - Cl; 372 (31.9) M - 2Cl; 337 (10.9) M - 3Cl; 301 (2.0) M - 4Cl; 271 (57.2) C₁₂H₁₀N₂CC₆H₅; 180 (100) C₆H₅NC₆H₅; 105 (5.2) C₆H₅NC; 91 (30.7) C₆H₅N; 77 (12.1) C₆H₅.

3.2.13 Preparation of tetrafluoro(N,N-diphenylbenzamidino)phosphorus(V) (12)

A sample of N,N-diphenylbenzamidine (0.110 g, 0.412 mmol), prepared by literature methods,² was placed into a small glass reaction vessel and dissolved in toluene. Then 183 mL of PF₅ (42 mm Hg, 0.41 mmol) was distilled into the reaction vessel at -196° C. The vessel was vacuum sealed and allowed to warm slowly to room temperature overnight. The vessel was opened and the volatiles pumped away, to leave a white solid (mp 188-195° C). Compound **12** was primarily characterized by ³¹P and ¹H NMR spectroscopy (see Section 5.1.3).

3.2.14 X-ray Data Collection

A clear, colorless crystal of C₁₅H₂₂Cl₃F₆N₂P (**5**), having an irregular shape with the approximate dimensions of 0.2 x 0.4 x 0.4 mm, was mounted in a capillary under a nitrogen atmosphere, and optically centered in the X-ray beam of an Enraf-Nonius CAD4 automated diffractometer. All intensity measurements were performed using Mo K α radiation ($\lambda = 0.71073$ Å) with a graphite crystal, incident beam monochromator.

The automatic peak search and reflection indexing programs³ generated a preliminary unit cell. An explorative survey of the crystal by oscillation and Weissenberg photography led to the final choice of a monoclinic cell with the systematic absences of $h0l$, l odd and $0k0$, k odd; the space group was chosen as $P2_1/c$ (No. 14).⁴

The cell constants and orientation matrix were obtained by a least-squares refinement of the setting angles of 25 reflections in the range $18.9 < \theta < 24.7^\circ$. The unit cell parameters are given in Table 3.1.

The intensity data were collected at room temperature (22° C) using a $\omega - 2\theta$ scan of fixed speed, $2.0^\circ \text{ min}^{-1}$ in θ . The scan range varied as a function of θ to compensate for $\alpha_1 - \alpha_2$ wavelength dispersion: $\text{omega scan width} = 1.00 + 0.35 \tan(\theta)^\circ$. Backgrounds for

Table 3.1 Crystal Data and Details of Intensity Collection

Cl ₂ (CF ₃) ₂ P(DCC)Cl (5)	
mol formula	C ₁₅ H ₂₂ Cl ₃ F ₆ N ₂ P
fw	481.68
cryst shape	plate
cryst size (mm)	0.2 x 0.4 x 0.4
systematic absences	<i>h</i> 0 <i>l</i> (<i>l</i> odd), 0 <i>k</i> 0 (<i>k</i> odd)
space group	monoclinic, <i>P</i> 2 ₁ / <i>c</i> (No. 14)
temp (°C)	22
radiation (λ, Å)	Mo Kα (0.71073)
unit cell parameters	
<i>a</i> (Å)	8.548 (3)
<i>b</i> (Å)	24.280 (8)
<i>c</i> (Å)	10.571 (5)
β (deg)	111.18 (3)
Volume (Å ³)	2045
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.564
linear abs coeff μ (cm ⁻¹)	2.99
max 2θ reflections	
collected (deg)	60
index range	(± <i>h</i> , + <i>k</i> , ± <i>l</i>)
takeoff angle (deg)	3.00
detector aperture (mm)	2.40 (horiz), 4.00 (vert)
cryst to detector dist (mm)	205
scan type	ω-2θ
scan rate (deg min ⁻¹)	2.0
scan width (deg)	1.00 + 0.35 tanθ
total reflcns collected, averaged	8936, 5935
no. of observs (<i>I</i> > 3σ(<i>I</i>))	2540
no. of variables	271
final <i>R</i> , <i>R</i> _w , GOF ^a	0.052, 0.067, 2.14

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2};$$

$$GOF = [\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$$

the peaks were measured by extending the scan 25% on each side; this gave a peak-to-background counting time ratio of 2:1. Intensity measurements were made out to a maximum 2θ of 60° . Two reflections were chosen as standard reflections, and were remeasured after every 120 min of exposure time to check on crystal and electronic stability over the course of data collection. The intensities of these reflections decreased overall by 7.2% and 10.9% during the data collection, but no decay correction was employed.

3.2.15 X-ray Data Reduction

A total of 8936 reflections were collected, and Lorentz and polarization factors were applied: $I = r(S - 2B)/L_p$; $s(I) = [r(S + 4B) + (0.041I)^2]^{1/2}/L_p$, where r is the scan rate, S is the total scan count, B is the total background count, and L_p is the combined Lorentz and polarization factor.

3.2.16 Structure Solution and Refinement

The positions of the P and Cl atoms were derived from a Patterson map, and the remaining non-hydrogen atoms were located from a difference Fourier map. Adjustment⁵ of atomic parameters was carried out by full-matrix least-squares refinement on F_o minimizing the function $\sum w (|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is given by $w = 4F_o^2 / \sigma^2(F_o^2)$.

The neutral atom scattering factors were calculated from the analytical expression for the scattering factor curves.⁶ The f' and f'' components of anomalous dispersion⁷ were included in the calculations of all non-hydrogen atoms.

All hydrogen atoms were generated at idealized calculated positions by assuming a C-H bond length of 0.95 Å and the appropriate sp^3 geometries. These atoms were then included in the calculations with fixed, isotropic Gaussian parameters 1.2 times that of the attached atom and constrained to 'ride' on this atom.

The refinement of the coordinates and isotropic U's for all non-hydrogen atoms was continued to convergence. At that stage, the data were corrected for absorption effects (and other systematic errors) using a scheme based on the absorption surface (Fourier filtering) method of Walker and Stuart.⁸ The maximum and minimum correction factors applied to F_0 were 1.3278 and 0.5548. After rejecting the systematically absent reflections and averaging over 2/m symmetry (R-merge on F for all data is 0.219), there were 5935 reflections of which 2540, having $I > 3\sigma(I)$, were used in the subsequent refinement. The refinement was continued with use of anisotropic Gaussian displacement parameters for the non-hydrogen atoms. One CF_3 group was found to be rotationally disordered, and was split into two groups of partial occupancy, 0.6 in one group (F11-F13) and 0.4 in the other (F14-F16). In the final cycle 271 parameters were refined using 2540 observations with $I > 3\sigma(I)$ with the largest and average shift/error less than 0.01. As a result, the goodness-of-fit was 2.14, and $R = \sum ||F_0| - |F_c|| / \sum |F_0| = 0.052$ and $R_w = (\sum w (|F_0| - |F_c|)^2 / \sum w F_0^2)^{1/2} = 0.067$. An analysis of R_w in terms of F_0 , $\sin \theta / \lambda$, and various combinations of Miller indices indicated no unusual trends. The highest peak in the final difference Fourier map has a density of 0.32(7) e Å⁻³.

The positional and isotropic thermal parameters for compound **5** are given in Tables 3.2 and 3.3. Additional information is available as supplementary material.⁹

3.3 Results and Discussion

Reactions of PX_5 ($X = F, Cl, CF_3$) with acetylacetone¹⁰ (Chapter 2) and 8-hydroxyquinoline¹¹ have provided an extensive series of five- and six-membered chelate

Table 3.2 Positional^a and Thermal^b Parameters for Cl₂(CF₃)₂P(DCC)Cl (5)

atom	x	y	z	U _{eq} ^c
P	1478 (1)	1368 (5)	3505 (1)	4.15 (3)
Cl(1)	594 (2)	1686.5 (7)	4980 (1)	7.37 (5)
Cl(2)	-911 (1)	1254.6 (6)	1955 (1)	5.85 (4)
Cl(3)	6073 (1)	1112.4 (6)	3528 (1)	6.91 (5)
N(1)	3733 (4)	1401 (2)	4535 (3)	4.5 (1)
N(2)	2702 (4)	1112 (1)	2513 (3)	3.9 (1)
C(11)	4767 (5)	1581 (2)	5929 (4)	5.6 (2)
C(12)	5737 (7)	2098 (2)	5973 (5)	6.6 (2)
C(13)	6614 (7)	2284 (3)	7448 (6)	8.8 (2)
C(14)	7761 (7)	1841 (3)	8270 (6)	8.9 (3)
C(15)	6827 (9)	1308 (3)	8205 (6)	11.6 (3)
C(16)	5927 (8)	1121 (2)	6741 (5)	8.9 (3)
C(21)	2336 (5)	896 (2)	1131 (4)	4.9 (2)
C(22)	3040 (7)	330 (2)	1105 (5)	7.2 (2)
C(23)	2420 (7)	106 (3)	-338 (5)	8.8 (2)
C(24)	2851 (7)	490 (3)	-1281 (5)	8.8 (2)
C(25)	2215 (9)	1060 (3)	-1216 (5)	10.9 (3)
C(26)	2824 (8)	1276 (2)	229 (5)	9.3 (2)
C(1)	1572 (5)	2116 (2)	2862 (5)	5.4 (2)
C(2)	1272 (6)	641 (2)	4151 (4)	5.9 (2)
C(3)	4104 (5)	1208 (2)	3527 (4)	4.3 (1)
F(11) ^d	121 (6)	2341 (2)	2073 (6)	9.4 (2)
F(12) ^d	2546 (6)	2181 (2)	2163 (5)	9.7 (2)
F(13) ^d	2142 (7)	2469 (2)	3875 (5)	8.6 (2)
F(14) ^d	1160 (11)	2107 (3)	1538 (7)	8.6 (3)
F(15) ^d	3050 (10)	2352 (3)	3275 (10)	10.9 (4)
F(16) ^d	539 (10)	2447 (4)	3030 (9)	12.8 (3)
F(21)	-176 (4)	543 (1)	4304 (3)	9.8 (1)
F(22)	2425 (4)	517 (2)	5325 (3)	10.6 (1)
F(23)	1350 (4)	239 (1)	3306 (3)	9.5 (1)

a Values x 10⁴.

b Values x 10³, Å².

c $U_{eq} = \frac{1}{3} \sum_{i=1}^3 r_i^2$, where r_i are the root-mean-square amplitudes of the anisotropic Gaussian displacement parameters.

d CF₃ group is disordered; partial population of 0.6 for atoms F(11)-F(13), 0.4 for F(14)-F(16).

Table 3.3 Hydrogen Atoms Positional and Thermal Parameters^a for
Cl2(CF3)2P(DCC)Cl (5)

atom	x	y	z	$U_{eq}^b, \text{\AA}^2$
H(11)	398	166	635	7
H(121)	499	238	548	8
H(121)	655	203	558	8
H(131)	579	236	783	11
H(132)	725	261	746	11
H(141)	823	196	919	11
H(142)	863	178	793	11
H(151)	602	136	862	14
H(152)	760	103	868	14
H(161)	673	104	634	11
H(163)	528	80	673	11
H(21)	115	87	77	6
H(221)	269	9	166	9
H(222)	423	35	144	9
H(231)	124	6	-65	11
H(232)	293	-24	-34	11
H(241)	236	36	-218	11
H(242)	404	50	-103	11
H(251)	102	105	-156	13
H(252)	260	130	-175	13
H(261)	401	131	56	11
H(262)	234	163	24	11

a All parameters have been multiplied by 10^3 .

b $U_{eq} = \frac{1}{3} \sum_{i=1}^3 r_i^2$, where r_i are the root-mean-square amplitudes of the anisotropic Gaussian displacement parameters.

rings of λ^6 -phosphorus derivatives. The formation of the potentially more strained four-membered ring systems has been of recent interest. This chelate behaviour of small-bite ligands has been shown in a few examples of carbamates,¹² urea,¹³ and benzamidines¹⁴. However, this list of four-membered ring phosphorus chelates is by no means extensive.

Most λ^6 -phosphoranes are synthesized from λ^5 -phosphoranes in three general ways:

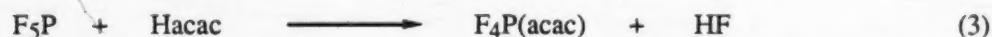
- i) a Lewis acid-base reaction,¹⁵



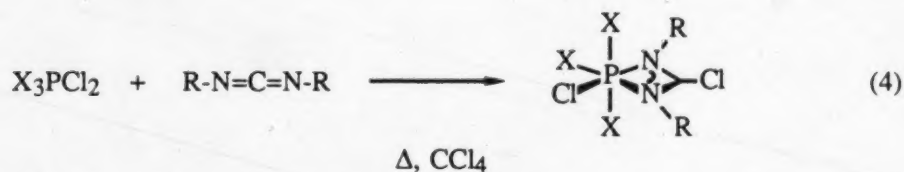
- ii) an apparent CO_2 insertion into a P-N bond,¹²



- or iii) a 1:1 substitution with a bidentate ligand.¹⁶



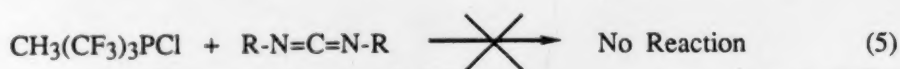
The preparative route for compounds **1-8**, apparent carbodiimide insertion into a P-Cl bond of a λ^5 -phosphorane to form a four-membered ring system, is novel. The compounds with hexacoordinate phosphorus (**1 to 8**) were prepared in quantitative yields by refluxing the phosphorane and carbodiimide in CCl_4 for a few hours (eq (4)).



R = cyclohexyl or isopropyl; X = Cl or CF_3

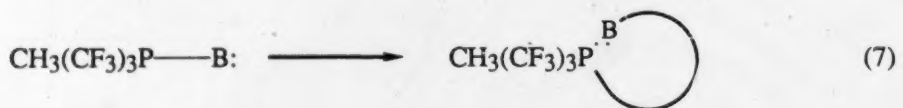
The resulting compounds were air stable, moisture sensitive, colorless and crystalline solids with sharp melting points ranging from 70 to 165° C. They were immediately identified as λ^6 -phosphoranes by their low frequency (high field) signals in the ^{31}P NMR spectra.

An attempt to generate λ^6 -phosphoranes from the tetraalkyl-monochlorophosphorane, $\text{CH}_3(\text{CF}_3)_3\text{PCl}$, via a similar reaction did not succeed, even after prolonged heating (eq (5)).



R = cyclohexyl or isopropyl

The failure of reaction was unexpected, considering that $\text{CH}_3(\text{CF}_3)_3\text{PX}$ (X = Cl or F) undergoes ready substitution (eq (3)) with monovalent chelate precursors, such as acetylacetone or $(\text{CH}_3)_3\text{SiO}_2\text{CN}(\text{CH}_3)_2$ (eqs (6) and (7)).



X = Cl, F; M = H, $\text{Si}(\text{CH}_3)_3$; B = O, S, N.

Perhaps the pathway to the final hexacoordinate product involves two chlorines on the phosphorus. Alternatively, as described in Chapter 2, steric hindrance around the central phosphorus can interfere with the formation of a six-coordinate phosphorus compound. It is possible that $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ is sufficiently more sterically hindered than $(\text{CF}_3)_3\text{PCl}_2$ or the other chlorophosphoranes used, so that the formation of the analogous hexacoordinate product is in this case blocked.

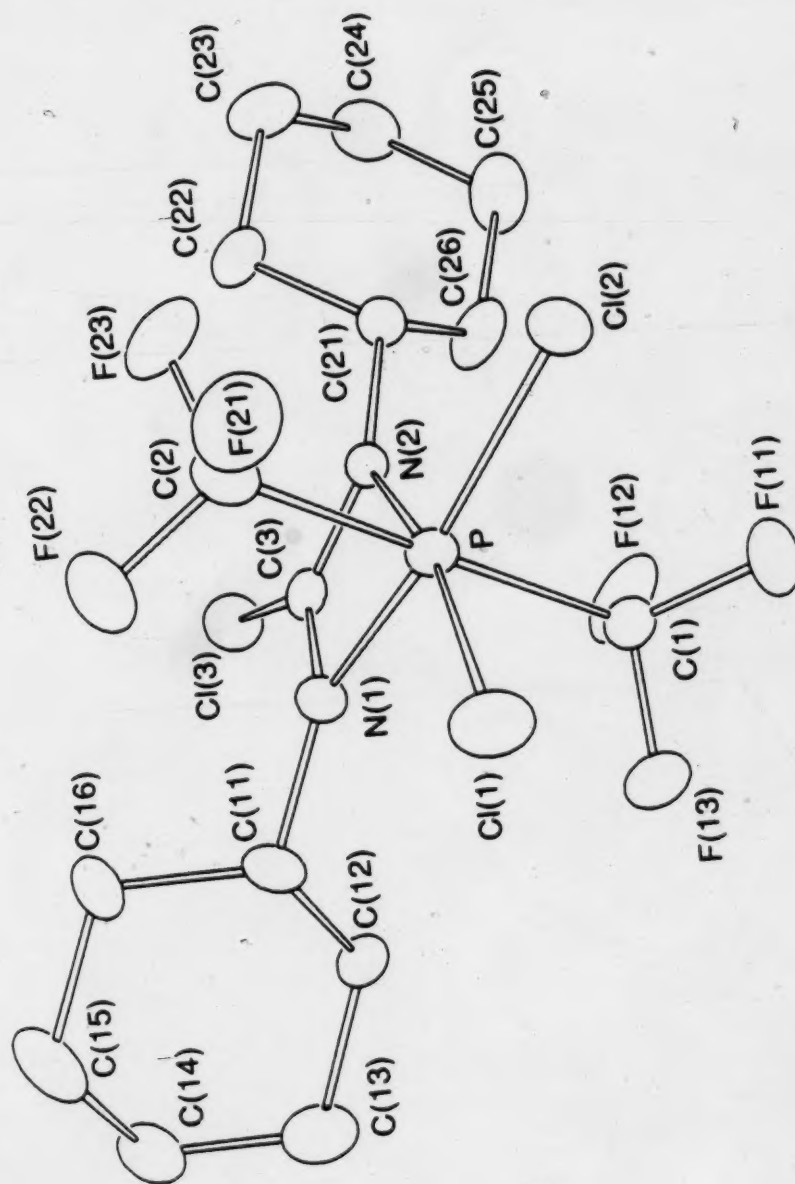


Figure 3.2 Perspective view of **5** showing the atom labelling scheme. Atoms are represented by Gaussian ellipsoids at the 30% probability level. For the disordered CF₃ group only the major occupancy is shown. Structure courtesy of Dr. B.D. Santarsiero.

3.3.1 Structure of $\text{Cl}_2(\text{CF}_3)_2\text{P}(\text{DCC})\text{Cl}$ (**5**)¹⁷

The structure of compound **5**, shown in Figure 3.2, has a six-coordinate environment at phosphorus. The two CF_3 groups are mutually trans in the axial positions and the two mutually cis chlorine atoms and the carbodiimide chelate occupy the radial positions. Relevant metrical parameters for compound **5** are given in Tables 3.4 and 3.5.

The structure of a related compound, $\text{Cl}_4\text{PN}(\text{CH}_3)\text{C}(\text{Cl})\text{NCH}_3$, prepared from PCl_5 and dimethylurea has been previously reported.¹⁸ However, severe problems with hydrolysis of the crystal were encountered during data collection resulting in a final structure refinement to an R factor of 0.13. Generally an R factor (a measurement of the error) greater than 0.10 is considered to be a poor value. The structure of **5** has a similar framework around phosphorus compared to the hexacoordinate acetylacetonate analog, $\text{Cl}_2(\text{CF}_3)_2\text{P}(\text{acac})$, which we have previously reported.¹⁰

As in the acetylacetonate analog, the trans positioning of the CF_3 groups is the sterically favoured structure, because the relatively bulky CF_3 groups may avoid any interaction with each other. The CF_3 groups are orthogonal to the radial plane formed by the phosphorus atom, the carbodiimide moiety, and the two chlorine atoms. The atoms in the radial section are essentially coplanar with the largest deviation from the least-squares plane being 0.012(5) Å for the C atom in the four-membered ring. The CF_3 groups, which sit above and below the phosphorus, bend slightly away from the sterically bulky carbodiimide ring side towards the radial chlorine atoms so as to form a C(1)-P-C(2) angle of 177.1(3)°. The large cyclohexyl groups are folded in an expected chair conformation and are positioned away from the phosphorus center, avoiding interaction with other atoms within the molecule (Figure 3.3).

Unlike the acetylacetonate analog, compound **5** deviates more from the ideal octahedral arrangement around the phosphorus. The small bite angle of the chelating carbodiimide ligand (70.3(2)°), compared to the acetylacetonate ligand (95.4(2)°), allows

Table 3.4 Bond Distances^a for Cl₂(CF₃)₂P(DCC)Cl (5)

atom 1	atom 2	dist	atom 1	atom 2	dist
P	Cl(1)	2.110 (2) ^b	N(1)	C(11)	1.483 (5)
P	Cl(2)	2.124 (2)	N(2)	C(21)	1.475 (5)
P	C(1)	1.950 (5)	C(11)	C(12)	1.496 (7)
P	C(2)	1.924 (6)	C(12)	C(13)	1.533 (8)
P	N(1)	1.841 (3)	C(13)	C(14)	1.503 (8)
P	N(2)	1.837 (4)	C(14)	C(15)	1.509 (9)
C(1)	F(11)	1.336 (6)	C(15)	C(16)	1.527 (8)
C(1)	F(12)	1.307 (8)	C(16)	C(11)	1.534 (7)
C(1)	F(13)	1.320 (7)	C(21)	C(22)	1.522 (7)
C(2)	F(21)	1.326 (6)	C(22)	C(23)	1.505 (7)
C(2)	F(22)	1.311 (5)	C(23)	C(24)	1.498 (9)
C(2)	F(23)	1.340 (6)	C(24)	C(25)	1.498 (10)
N(1)	C(3)	1.305 (6)	C(25)	C(26)	1.517 (7)
N(2)	C(3)	1.308 (4)	C(26)	C(21)	1.493 (8)
C(3)	Cl(3)	1.698 (5)			

^a In angstroms.^b Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 3.5 Bond Angles^a for Cl₂(CF₃)₂P(DCC)Cl (5)

atom 1	atom 2	atom 3	angle
Cl(1)	P	Cl(2)	96.67 (8) ^b
Cl(1)	P	C(1)	89.3 (2)
Cl(1)	P	C(2)	88.3 (2)
Cl(1)	P	N(1)	97.2 (1)
Cl(1)	P	N(2)	167.4 (1)
Cl(2)	P	C(1)	90.1 (1)
Cl(2)	P	C(2)	88.2 (1)
Cl(2)	P	N(1)	166.2 (1)
Cl(2)	P	N(2)	95.9 (1)
Cl(3)	P	C(2)	176.9 (2)
Cl(3)	P	N(1)	90.0 (2)
Cl(3)	P	N(2)	90.7 (2)
C(2)	P	N(1)	92.3 (2)
C(2)	P	N(2)	92.1 (2)
P	C(1)	F(11)	116.9 (4)
P	C(1)	F(12)	115.2 (4)
P	C(1)	F(13)	111.9 (4)
P	C(1)	F(14)	109.2 (5)
P	C(1)	F(15)	116.6 (4)
P	C(1)	F(16)	115.4 (6)
F(11)	C(1)	F(12)	103.6 (5)
F(11)	C(1)	F(13)	103.1 (5)
F(12)	C(1)	F(13)	104.8 (5)
P	C(2)	F(21)	114.6 (3)
P	C(2)	F(22)	114.3 (3)
P	C(2)	F(23)	113.5 (3)
F(21)	C(2)	F(22)	105.0 (4)
F(21)	C(2)	F(23)	103.0 (4)
F(22)	C(2)	F(23)	105.3 (4)
P	N(1)	C(3)	90.7 (2)
P	N(1)	C(11)	136.1 (3)
C(3)	N(1)	C(11)	133.1 (4)
P	N(2)	C(3)	90.8 (3)
P	N(2)	C(21)	136.5 (3)
C(3)	N(2)	C(21)	132.7 (4)
N(1)	C(3)	N(2)	108.2 (4)
N(1)	C(3)	Cl(3)	125.6 (3)
N(2)	C(3)	Cl(3)	126.2 (4)
N(1)	C(11)	C(12)	113.8 (4)
N(1)	C(11)	C(16)	112.0 (4)

... Table 3.5 Continued. Bond Angles^a for Cl₂(CF₃)₂P(DCC)Cl (5)

atom 1	atom 2	atom 3	angle
C(12)	C(11)	C(16)	110.8 (4)
C(11)	C(12)	C(13)	109.9 (5)
C(12)	C(13)	C(14)	110.8 (5)
C(13)	C(14)	C(15)	111.3 (5)
C(14)	C(15)	C(16)	111.5 (5)
C(11)	C(16)	C(15)	109.8 (5)
N(2)	C(21)	C(22)	113.6 (3)
N(2)	C(21)	C(26)	113.8 (4)
C(22)	C(21)	C(26)	110.3 (5)
C(21)	C(22)	C(23)	110.3 (4)
C(22)	C(23)	C(24)	111.3 (5)
C(23)	C(24)	C(25)	111.2 (5)
C(24)	C(25)	C(26)	111.6 (4)
C(21)	C(26)	C(25)	110.8 (5)

^a In degrees.

^b Numbers in parentheses are estimated standard deviations in the least significant digits.

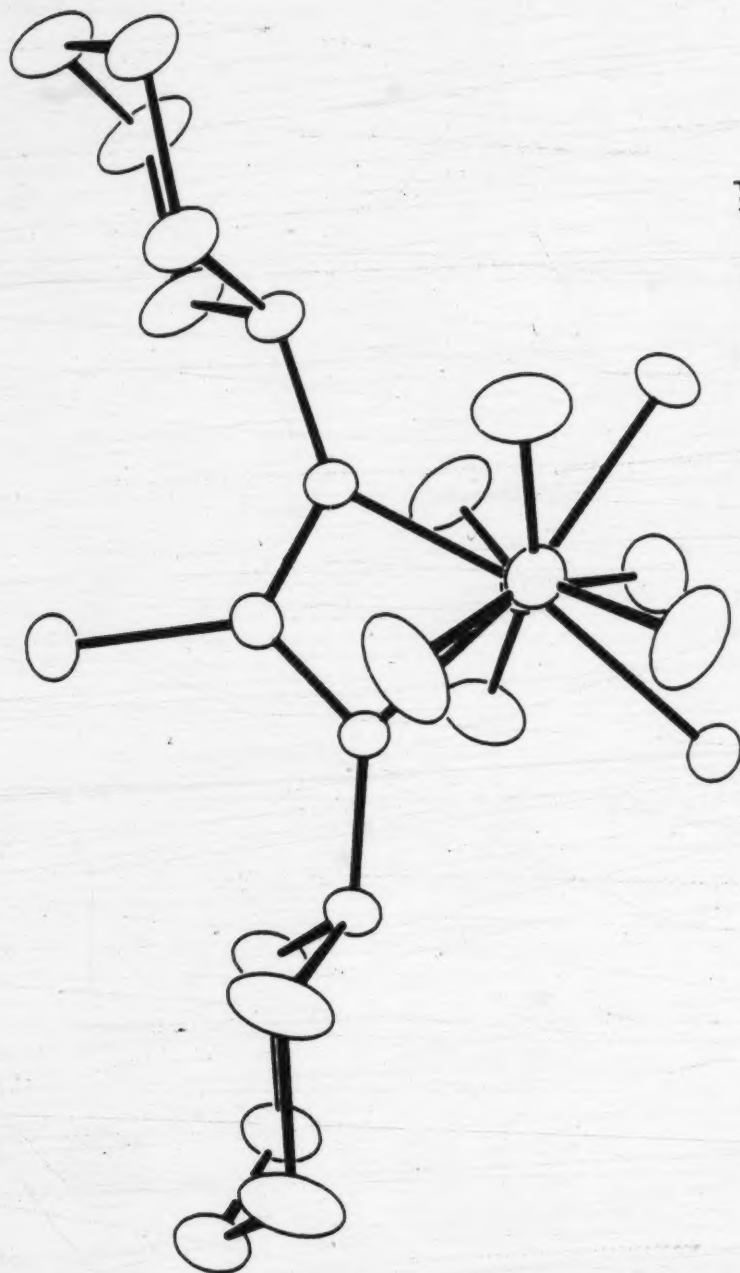


Figure 3.3 Perspective view of 5 along the axial bonds. Atoms are represented by Gaussian ellipsoids at the 30% probability level.
Structure courtesy of Dr. B.D. Santariero.

more room for the chlorines to spread out around the phosphorus and form 96° angles in the radial plane, instead of the ideal 90° . This deviation from a true octahedral framework has been observed before in other neutral hexacoordinate phosphorus compounds such as the dimethylcarbamates, $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)^{19}$ and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)^{12}$ which also contain a bidentate ligand with a very small bite size (72.4° and 69.9° , respectively).

Both the P-Cl and the P-C bond distances are normal with means of $2.116 \text{ \AA}$ and $1.912 \text{ \AA}$, respectively. The ring C-Cl distance ($1.696(6) \text{ \AA}$) is very similar to the distance expected for a C-Cl single-bond ($1.70 \text{ \AA}$) found in olefinic and aromatic compounds. Although the C-N bonds between the cyclohexyl groups and the nitrogens are comparable to the average single-bond C-N distance of $1.45 \text{ \AA}$, the ring C-N bonds are significantly smaller ($1.310 \text{ \AA}$), indicating the presence of a delocalized double bond within the N-C-N ring system.

The most remarkable feature of this structure is the planarity and delocalization of this chelating ring. The structure of **5**, and in general any compound in this carbodiimide series, can be represented as two resonance forms.



Cy = cyclohexyl

The ring C-N bond is a partial double bond, as evidenced by its shorter bond length. In addition, the presence of a dative N:-P bond in the resonance structures is reflected in the longer P-N bond distance of $1.830 \text{ \AA}$, compared to the expected P-N single-bond distance of $1.78 \text{ \AA}$.

3.3.2 Structure of $\text{Cl}(\text{CF}_3)_3\text{P}(\text{DCC})\text{Cl}$ (7)⁷

The structure data for **7** was collected by Dr. B. Vaartstra and the structure solution was carried out by the author under the supervision of Professor M. Cowie. The structure of compound **7** showed a space group ambiguity and severe disordering so refinement was not continued. However, it is clear from the structure even at this poorly refined stage that compound **7** contains a hexacoordinate phosphorus with two axial CF_3 groups and one radial CF_3 group, similar to the carbamate analogs $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{NC}(\text{CH}_3)_2)^{19}$ and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{NC}(\text{CH}_3)_2)^{12}$. As in compound **5**, the axial CF_3 groups in **7** sit above and below the radial plane formed by the third CF_3 group, the chlorine, and the carbodiimide chelating ligand. The radial CF_3 group and Cl are positionally disordered and all the CF_3 groups are rotationally disordered. In addition, the cyclohexyl groups in **7** are in an expected chair conformation similar to **5**.

3.3.3 Nuclear Magnetic Resonance Spectra

The structures of compounds (**1-10**) could also be deduced from their ^1H , ^{19}F and ^{31}P NMR spectra. Examples are shown in Figure 3.1. A summary of the NMR parameters of compounds **1** to **10** is given in Table 3.6. Like the acetylacetonates with hexacoordinate phosphorus centers, the carbodiimides are not fluxional at room temperature, making characterization via NMR straightforward. The ^{31}P NMR spectra show, in all cases, chemical shifts at very low frequencies [-155 to -205 ppm] compared to the five-coordinate precursors $(\text{CF}_3)_n\text{PCl}_{4-n}$ ($n = 0-3$) [-56 to -80 ppm], indicating the formation of a hexacoordinate phosphorus center.

Compounds **1** and **2** are clearly characterized by the presence of a triplet ($^3J_{\text{PH}}$) signal at -205 ppm in the ^{31}P NMR spectra, due to the proton nearest to the phosphorus.

Table 3.6 NMR Parameters for (Carbodiimide)phosphoranes

Cmpd ^a	δ ¹ H ^b	ϕ ¹⁹ F ^c	σ ³¹ P ^d	³ J _{PH}	² J _{FP}	³ J _{HH}	⁴ J _{FF}
	Coupling Constants (Hz)						
1	4.12	—	-204.7 ^e	34.6	—	12.0 3.8	—
2	4.50	—	-205.2 ^e	34.8	—	7.0	—
3	4.08	-68.7 ⁱ	-181.7 ^f	20.7	134.0	m	—
4	4.50	-69.1 ⁱ	-181.8 ^f	20.4	134.0	6.9	—
5	3.91	-66.8 ⁱ	-155.8 ^g	10.2	170.5	11.9 4.0	—
6	4.34	-67.4 ⁱ	-155.7 ^g	10.0	171.6	7.0	—
7	3.66	-64.5 ^j (2) ^k -58.7 ^l (1) ^k	-154.9 ^h	9.6	128.4(ax) 82.1(rad)	12.0 4.0	12.6
8	4.09 4.30	-64.8 ^j (2) ^k -59.0 ^l (1) ^k	-155.3 ^h	9.2	128.4(ax) 82.9(rad)	7.0	12.6
9	4.53	—	-205.6 ^e	36.0	—	7.2	—
10	3.85 4.28	—	-10.5 ⁱ	18.1	—	6.3 6.8	—

- a in CDCl₃
 b ppm relative to TMS
 c ppm relative to CFCl₃
 d ppm relative to 85% H₃PO₄
 e triplet
 f quartet of triplets
 g septet of triplets
 h septet of quartets of triplets
 i doublet
 j doublet of quartets
 k relative intensity
 l doublet of septets
 m signal too broad to determine HH coupling

This proton resides on the cyclohexyl or isopropyl group on each of the nitrogens of the chelating bidentate ligand.

As expected, compounds **3** and **4** display a low frequency quartet of triplets ($^2J_{\text{PF}}$ and $^3J_{\text{PH}}$ respectively) in the ^{31}P NMR spectra. The lone CF_3 group must necessarily lie in the axial position, because there is only one phosphorus coupled signal in the ^1H NMR spectra indicating a symmetry plane orthogonal to the plane of the $\overline{\text{PNCN}}$ ring.

The appearance of a clean doublet in each of the ^{19}F NMR spectra for compounds **5** and **6** shows that the CF_3 groups are chemically equivalent and therefore in symmetrical positions. Consequently, the CF_3 groups in compounds **5** and **6** may lie in both axial or both radial positions to account for the doublet in the ^{19}F NMR and the lone proton (phosphorus coupled) signal in the ^1H NMR spectra. In the analogous compounds $\text{F}_2(\text{CF}_3)_2\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ ($^2J_{\text{PF}} = 164.3 \text{ Hz}$)¹² and $\text{F}_2(\text{CF}_3)_2\text{P}(\text{acac})$ ($^2J_{\text{PF}} = 163.4 \text{ Hz}$)¹⁰ the two CF_3 groups lie solely in the axial positions and display a similarly large $^2J_{\text{PF}}$ coupling compared to compounds **5** and **6** ($^2J_{\text{PF}} = 171 \text{ Hz}$). Therefore, it seems most likely that the CF_3 groups in compounds **5** and **6** are also in the axial positions. Finally, the most convincing evidence is the solid state structure of **5**, which also shows the CF_3 groups to be in the axial positions.

The low frequency chemical shifts of **7** and **8** in the ^{31}P NMR spectra indicate hexacoordination about phosphorus. The phosphorus signals in **7** and **8** are split into a first-order septet of quartets with $^2J_{\text{PF}}$ coupling to three CF_3 groups. The nature of the splitting pattern suggests that **7** and **8** have two different CF_3 groups in a 2:1 ratio. The ^{31}P NMR spectrum (no ^1H decoupling) of **8**, shown in Figure 3.4, illustrates this coupling pattern. Additional proton coupling is also seen, with each peak in the septet of quartets appearing as a triplet corresponding to $^3J_{\text{PH}}$ coupling to two isopropyl groups. In short, from the ^{31}P NMR spectrum we deduce that **7** and **8** are hexacoordinate phosphorus compounds with a carbodiimide chelate coordinating through both nitrogens, and three CF_3 groups in a 2:1 ratio.

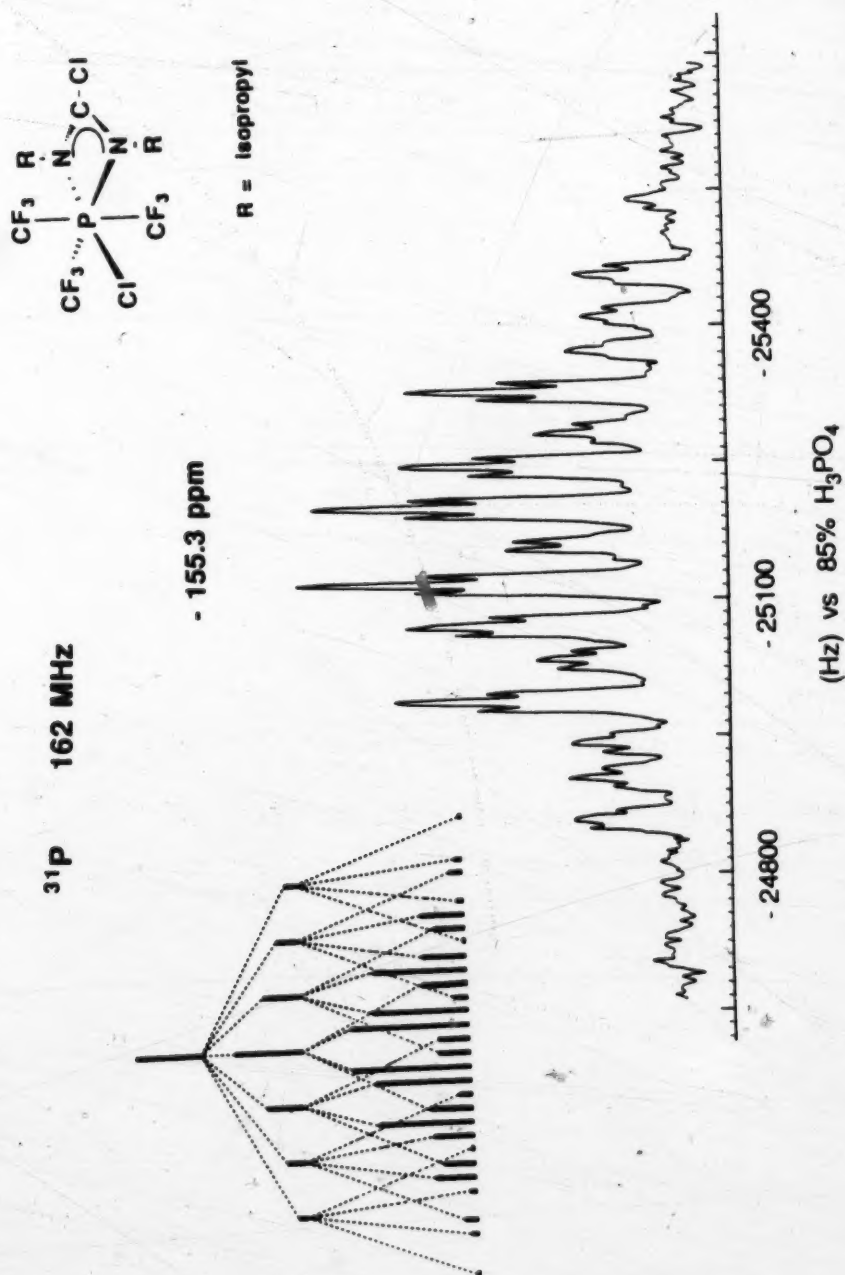


Figure 3.4 The ^{31}P NMR spectrum of $\text{Cl}(\text{CF}_3)_3\text{P}(\text{DPC})\text{Cl}$ (8) and its $^2J_{\text{PF}}$ coupling pattern.

The ^{19}F NMR spectra of compounds **7** and **8** show two signals in an intensity ratio of 2:1 with the expected doublet of quartets and doublet of septets, respectively (Figure 3.5). The signals arising from the two CF_3 groups have a larger $^2J_{\text{PF}}$ coupling constant of about 128 Hz compared with the remaining CF_3 signal, which has a $^2J_{\text{PF}}$ coupling constant of about 82 Hz. In previously prepared hexacoordinate phosphorus compounds with similar structures containing three CF_3 groups and a bidentate ligand, the $^2J_{\text{PF}}$ coupling constants of the axial CF_3 groups are equal to or larger than those of the radial CF_3 group. For example, the carbamate $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ has $^2J_{\text{PF}}$ coupling constants of 95 Hz (axial) and 70 Hz (radial),¹² and $\text{F}(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ has $^2J_{\text{PF}}$ coupling constants of 141.5 Hz (axial) and 97.5 Hz (radial).¹⁹ This suggests that similar to other *cis*- CF_3 compounds containing hexacoordinate phosphorus that we have studied, there are two axial CF_3 groups and one radial CF_3 group in **7** and **8**.

In addition, the ^1H NMR spectrum has two distinct phosphorus coupled signals, which would support the structure shown in Figure 3.1. That is, two separate signals arising from protons *trans* to a CF_3 group and *trans* to Cl are observed. The ^1H NMR spectrum of **8**, shown in Figure 3.6, has two methyl signals at 1.5 ppm. In the expansion of the methyl region (Figure 3.6), we observe two doublets corresponding to two different isopropyl group environments. Further downfield (4.0-4.5 ppm region) there are two smaller individual multiplets. They correspond to the central proton on the two isopropyl groups and are expanded in Figure 3.7. Each signal is an expected septet in the ^{31}P decoupled spectrum, which corresponds to coupling to six equivalent methyl protons. In the ^{31}P coupled spectrum, each signal becomes an overlapping doublet of septets. This multinuclear NMR evidence shows the ligand isopropyl groups to be inequivalent and strongly suggests that **7** and **8** have two axial CF_3 groups and one radial CF_3 group in solution. Finally, the results of the X-ray structure of **7** indicate two axial CF_3 groups and one radial CF_3 group in the solid state.

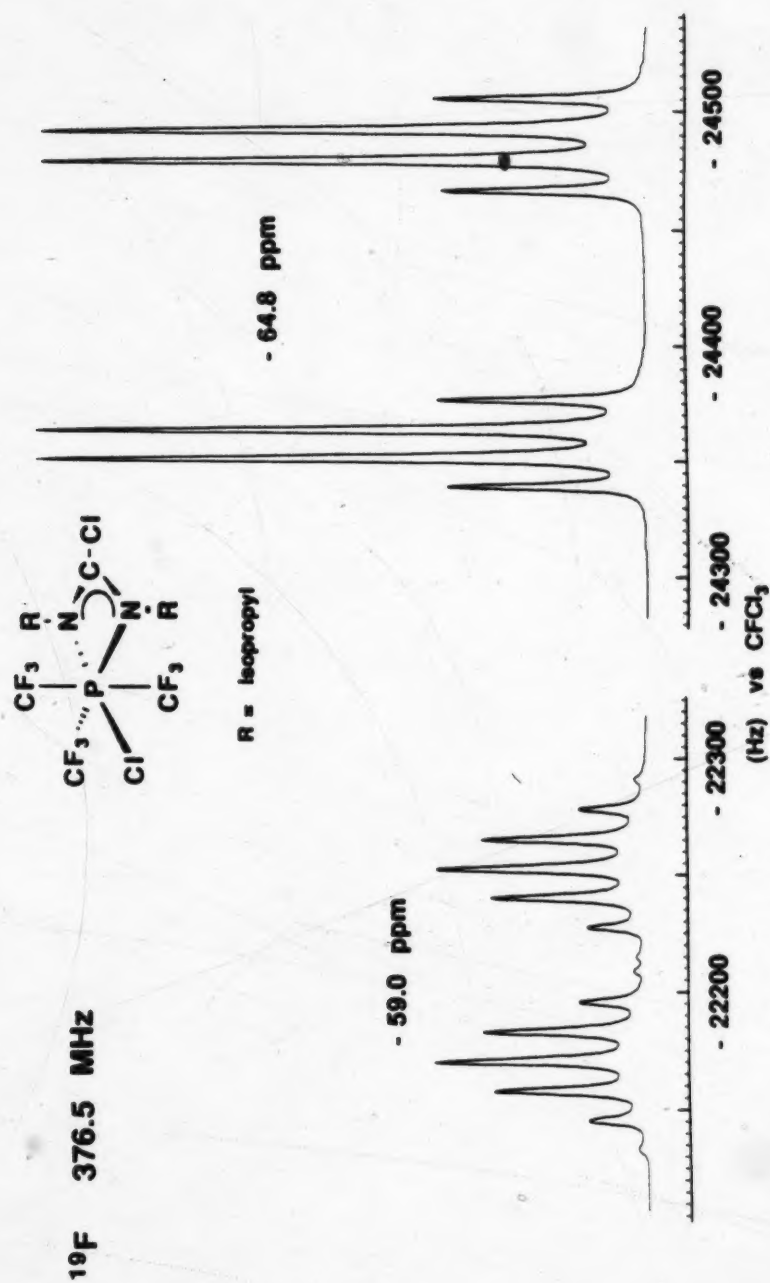


Figure 3.5 The ^{19}F NMR spectrum of $\text{Cl}(\text{CF}_3)_3\text{P}(\text{DPC})\text{Cl}$ (8).

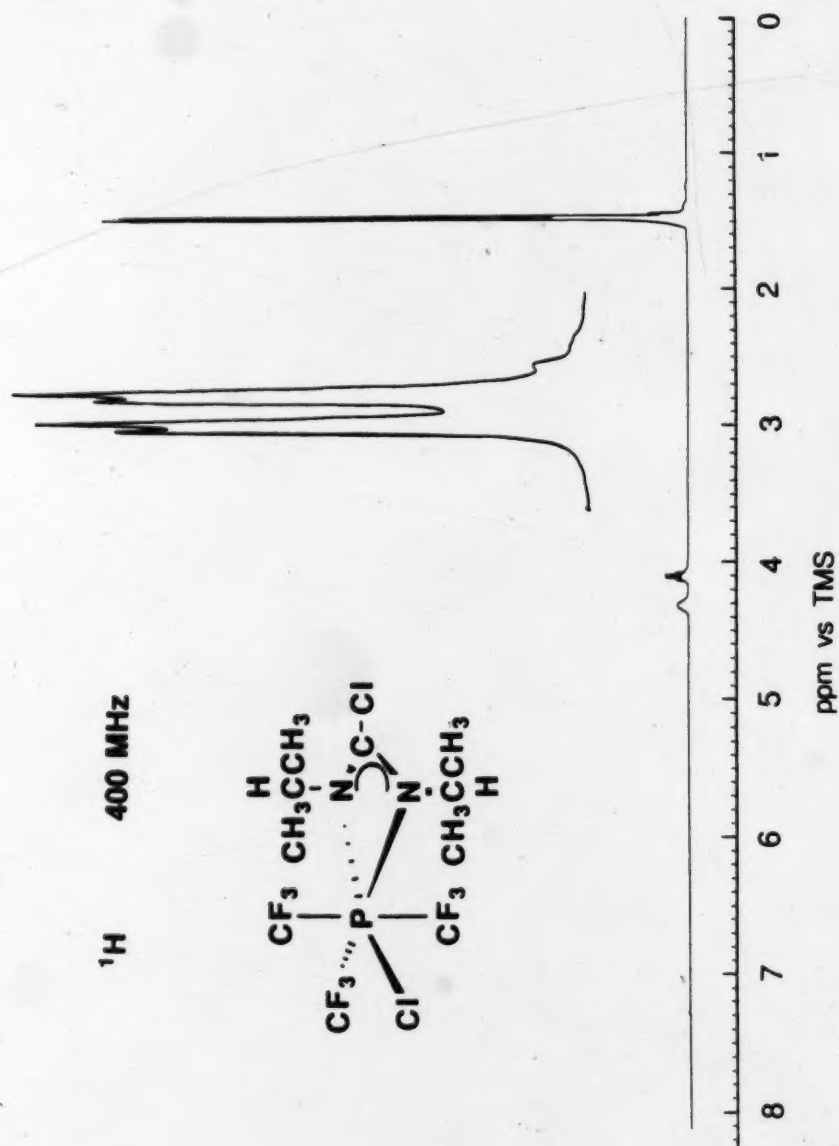


Figure 3.6 The ^1H NMR spectrum of $\text{Cl}(\text{CF}_3)_3\text{P}(\text{DPC})\text{Cl}$ (8).

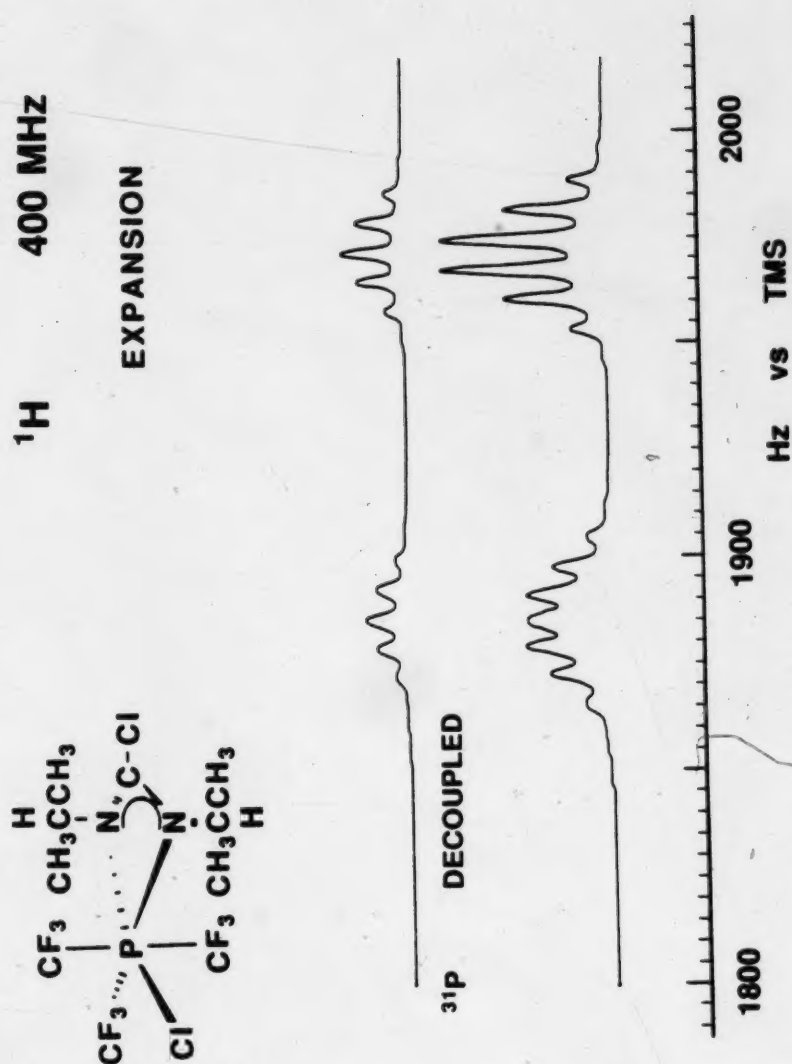


Figure 3.7 Expansion of R₃C-H region of Cl(CF₃)₃P(DPC)Cl (8)
¹H NMR spectrum.

Compounds **9** and **10** are products of a reactivity study done on **2** (presented separately in Results and Discussion 3.3.5) and have been primarily characterized by ^1H and ^{31}P NMR spectroscopies.

The ^{31}P NMR spectrum of **9** indicates the presence of a hexacoordinate phosphorus center with a low-frequency signal resonating as a triplet at -205.6 ppm. The $^3\text{J}_{\text{PH}}$ coupling to both isopropyl groups indicates that both nitrogens are still bound to the phosphorus. The ^1H NMR spectrum of **9** shows two equivalent isopropyl groups (coupled to phosphorus), implying a symmetrical compound, and one phenyl group (no phosphorus coupling). Together, the ^1H and ^{31}P NMR spectra indicate **9** to be the structure shown in Figure 3.1, where the phenyl group is attached to the ring carbon.

Compound **10** (the hydrolysis product of **2**) is a phosphoryl compound as evidenced by its ^{31}P NMR chemical shift of -10.5 ppm ($\text{Cl}_3\text{P}=\text{O}$ resonates at -2 ppm)²⁰ However, this phosphorus signal is a doublet, indicating coupling to only one isopropyl group. The ^1H NMR spectrum indicates two different isopropyl groups, only one of which is coupled to the phosphorus. This evidence supports the structure shown in Figure 3.1 for compound **10**.

3.3.4 Mass Spectra

The major mass spectral peaks observed for the (carbodiimide)phosphoranes are given in the Experimental section. As a four-coordinate center, **10** shows a parent ion. None of the compounds containing highly coordinated phosphorus (**1-9**) show a parent peak in the mass spectrum. All have major fragments identified as being due to a loss of one Cl from the parent molecule, apart from (**10**). Many of the other major peaks are generally attributed to the loss of the carbodiimide ligand and successive losses of Cl and CF_3 groups.

3.3.5 Infrared Spectra

The infrared absorption frequencies for compounds **1** to **10** are reported in Table 3.7. Of particular interest are the N=C stretching absorptions shown in Table 3.8. The large reduction in the N=C stretching frequency from the free ligand ($\sim 2100\text{ cm}^{-1}$) to the coordinated ligand ($\sim 1520\text{ cm}^{-1}$) supports the proposed structures. The bonding of the central C with the two coordinating nitrogens is a partial double bond with an absorption falling between a double ($\sim 2100\text{ cm}^{-1}$) and a single ($\sim 1350\text{ cm}^{-1}$) carbon-nitrogen bond. The analogous Mo and Re carbodiimides²¹ show higher N=C absorption frequencies, at 1644 and 1640 cm^{-1} , respectively, indicating the binding of the carbodiimide ligand to P is stronger than that shown by either the Mo or Re metal. This is also reflected in the shorter P-N bond length found in **5** ($1.839(4)\text{ \AA}$) compared to the longer Mo-N bond length in $\text{Cl}_4\text{Mo}(\text{DPC})\text{Cl}$ ($2.079(4)\text{ \AA}$).²¹ No significant difference was found in the N=C absorptions frequencies between $\text{Cl}_4\text{P}(\text{DPC})\text{Cl}$ (**2**) [1528 cm^{-1}] and $\text{Cl}_4\text{P}(\text{DPC})\text{Ph}$ (**9**) [1526 cm^{-1}]. Finally, as the number of CF_3 groups increases about the phosphorus, making it a stronger Lewis acid, the N=C frequency becomes slightly smaller, implying a stronger P-N bond.

3.3.6 Discussion of (N,N-diphenylbenzamidine) λ^6 -phosphoranes

The ^{31}P NMR spectrum of **11** has the characteristic low-frequency chemical shift (-184.6 ppm) for a hexacoordinate compound. The ^1H NMR spectrum has multiplet signals in the 6.90 to 7.65 ppm region corresponding to the phenyl protons. The ^{31}P and ^1H NMR data agree well with that for a series of analogous hexacoordinate (benzamidine)phosphoranes of the general formula $\text{Cl}_4\text{PN}(\text{Me})\text{C}(\text{Ph})\text{NR}$ ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{iso-C}_3\text{H}_7, \text{tert-C}_4\text{H}_9, \text{C}_6\text{H}_5$), which have been recently reported.²²

Table 3.7 Infrared Absorption Frequencies (cm⁻¹) for (Carbodiimide)phosphoranes.^a

1	2	3	4	5	6	7	8	9	10
2920 vs	2990 s	2960 vs	2970	2920 s	2980	2920 s	2975	2990 s	3200 br
2850 vs	2930	2880 s	2915	2845 s	2920	2810	2950	2930 vs	2982 s
1668	2880	2104	2850	1654	2860	2360	2900	2870 s	2944
1522 vs	1668	1679 s	1664	1516 vs	2330	2100	2845	1657 s	2875
1461	1528 vs	1519 vs	1524 vs	1462	1670	1654	2320	1526 vs	2536 br
1452 vs	1450	1467	1455	1452 s	1524 vs	1516 vs	1523 vs	1463	1682 vs
1369 s	1387	1452	1388	1366	1500	1487	1500 s	1453	1660 vs
1348	1366 s	1364	1368	1352	1465	1448	1461	1439	1611 vs
1327	1343	1351	1351	1268	1392	1370	1393	1386	1471
1289	1289	1258	1318	1174 s	1372	1339	1372	1369	1452
1261	1212 vs	1184	1212 s	1161 vs	1351	1256	1354	1343	1422
1181 s	1169	1156 s	1161 s	1131 vs	1211 s	1190 s	1206 s	1284 s	1400
1146	1131	1138	1145 s	1038	1166 vs	1174 vs	1186 vs	1236	1379
1080	1122 s	1121 s	1130 vs	1029	1137 vs	1166 vs	1168 vs	1212 s	1276 br vs
1047 s	931	1111 s	1121 vs	929	1128 vs	1143 vs	1143 vs	1152	1222 br
1024	699	1032	921	894	1068	1122 vs	1125 vs	1119 s	1167
946	654 s	1022	675	848	957	1078	1078	1027	1134
892	585	890	570 s	835	800	1028	919	1011	1118
839	533	708	520 s	693	793	1012	732	928	1079 s

... Table 3.7 continued.

1	2	3	4	5	6	7	8	9	10
814	517 vs 466 vs 438 vs	660 550 507 s 480 s		664 552 525 s 497 s 455 s	778 772 760 749 680 556 531 s 495 vs 460 s	922 887 848 691 671 s 562 s 499 s 463	682 s 570 s 498 s 472	656 614 588 556 s 546 s 539 s 516 vs 465 s 434 vs	563 vs

a In CCl₄ using 0.1 mm KBr solvent cell.

vs = very strong
s = strong
br = broad

Table 3.8 C=N Stretching Frequencies^a

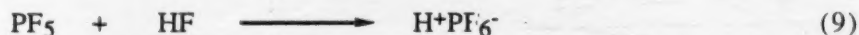
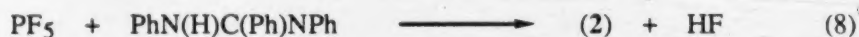
Compound	Frequency (cm ⁻¹)
DCC	2133
1	1522
3	1519
5	1516
7	1516
DPC	2112
Cl ₄ Mo(DPC)Cl ²¹	1644
Cl ₄ Re(DPC)Cl ²¹	1640
2	1528
4	1524
6	1523
8	1523
9	1526
10	1682

^a In CCl₄ using 0.1 mm KBr solvent cell.

DCC = dicyclohexylcarbodiimide
DPC = diisopropylcarbodiimide

The ^1H NMR spectrum of **12** shows the expected phenyl proton signals (6.72 to 7.23 ppm). However, the ^{31}P NMR spectrum indicates the presence of two major products, namely the expected $\text{F}_4\text{PN}(\text{Ph})\text{C}(\text{Ph})\text{NPh}$ (54%) which appears as a pentet ($^1J_{\text{PF}} = 849$ Hz) at -135.6 ppm, and the by-product HPF_6 (46%) which appears as a septet ($^1J_{\text{PF}} = 711$ Hz) at -144.2 ppm. The title compound is a neutral hexacoordinate compound with fluxional fluorines. Previous ^{31}P NMR studies of the analogous $\text{F}_4\text{PN}(\text{Me})\text{C}(\text{Ph})\text{NMe}$ indicate ring opening to a λ^5 -phosphorus intermediate to allow fluorine exchange. The free energy of activation for this process was calculated to be 23.6 kcal/mol.²³ Similar fluxional behavior has been reported in other neutral hexacoordinate phosphorus compounds such as the (dimethylcarbamato)phosphoranes²⁴ and the substituted (pyridinol)phosphoranes (Chapter 4), which both also contain a strained four-membered chelating ring.

The HPF_6 by-product is a result of HF eliminated in the initial reaction (eq. (8)), which reacts with PF_5 (eq. (9)).



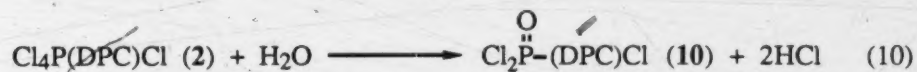
The PF_6^- species is thermodynamically a very stable entity. As a result, **12** cannot be isolated from the PF_6^- . By using a silylated form of the N,N-diphenylbenzamidine ligand (similar to the silylated pyridinol ligands used in Chapter 4), one would eliminate the generation of HF and hence the formation of the HPF_6 by-product.

In addition to preparation of the silylated benzamidine ligand, work is under way to react this benzamidine ligand with more sterically demanding phosphoranes, such as $\text{CH}_3(\text{CF}_3)_3\text{PCl}$. Successful formation of the hexacoordinate $\text{CH}_3(\text{CF}_3)_3\text{PN}(\text{Ph})\text{C}(\text{Ph})\text{NPh}$ by this route would indicate that the lack of reaction between $\text{CH}_3(\text{CF}_3)_3\text{PCl}$ and the

carbodiimides (DCC, DPC) is not merely a matter of steric hindrance. Conversely, no reaction in this case or formation of the λ^5 -phosphorane, would support the steric hindrance theory.

3.3.7 Reactivity of λ^6 -(carbodiimide)phosphoranes

The title compounds (1-8) are all thermally stable solids with melting points ranging from 70 to 170° C. They are extremely moisture sensitive, hydrolyzing to a yellow liquid (a λ^4 -phosphoryl derivative) when exposed to air. To illustrate this, when $\text{Cl}_4\text{P}(\text{DPC})\text{Cl}$ (2) is exposed to the moisture in the air or alternatively hydrolyzed directly with one equivalent of water (see Experimental 3.2.11) $\text{Cl}_2(\text{O})\text{P}(\text{DPC})\text{Cl}$ (10) is generated (eq.(10)).



Compound 10 has been characterized by ^{31}P and ^1H NMR spectroscopies (Table 3.6 and detailed in Results and Discussion 3.3.3), infrared spectroscopy (Table 3.7 and 3.8), mass spectroscopy and elemental analysis (Experimental 3.2.4). However, apart from their reactivity to water, these hexacoordinate phosphorus compounds (1-8) are surprisingly unreactive.

Reagents were chosen to evaluate nucleophilic and electrophilic reactivities in an attempt to study the chemistry of these compounds. Compound 2 was used as a model in a series of reactions (summarized in Figure 3.8). Although the synthesis and characterization of λ^6 -phosphorus compounds has been prevalent to date, this is the first reaction study that has been carried out on neutral λ^6 -phosphorus compounds. Several reagents were used, including well-established silylating and methylating agents. As illustrated in Figure 3.8,

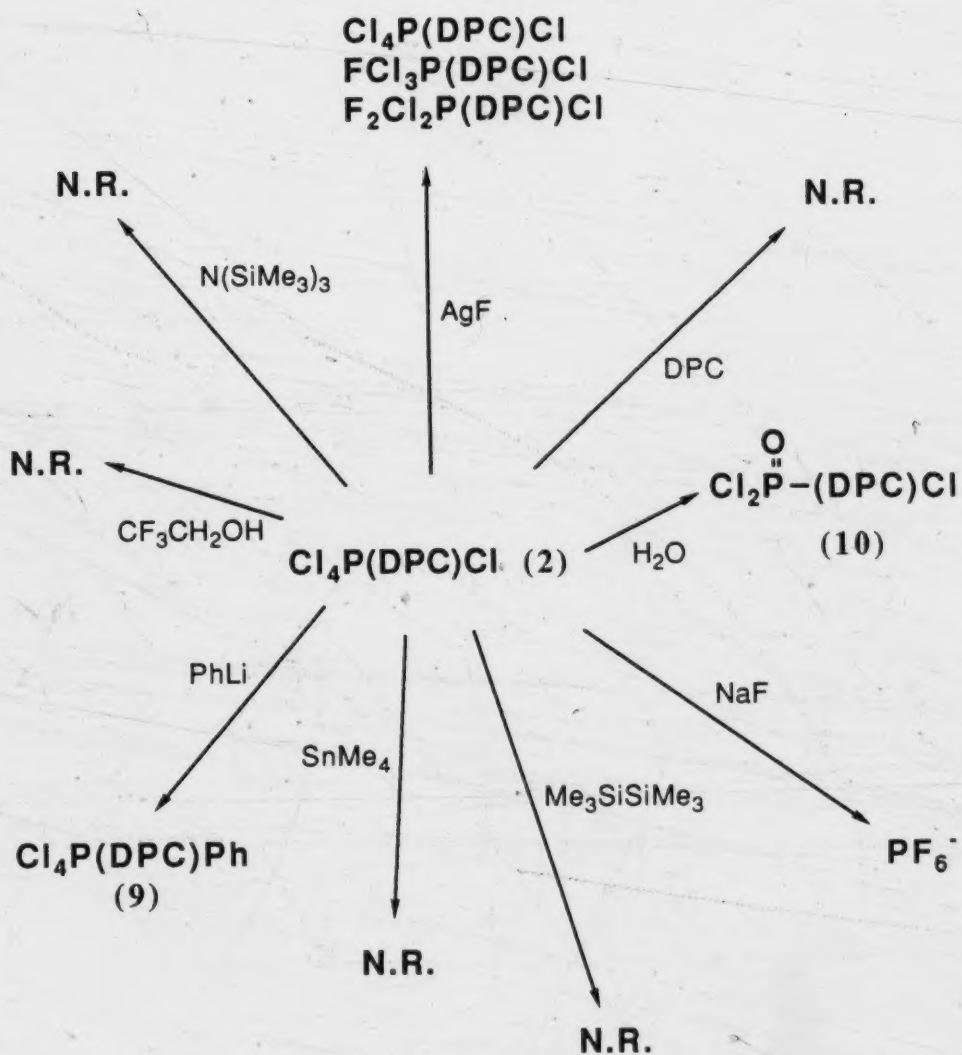
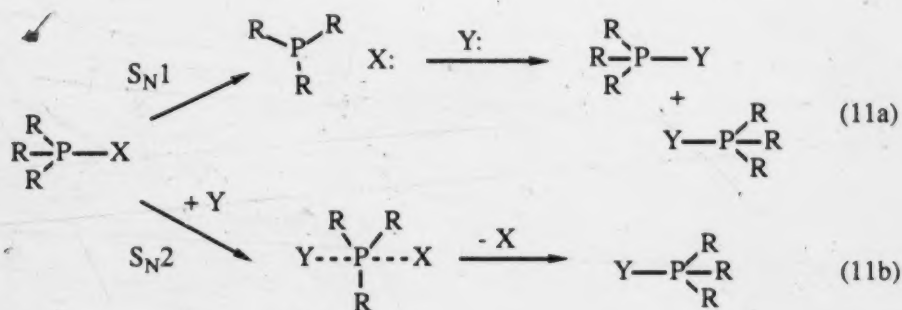


Figure 3.8 Some reactions of $\text{Cl}_4\text{P}(\text{DPC})\text{Cl} \quad (2)$.

compound 2 is resistant to simple nucleophilic substitution of its chlorines. The lack of reactivity of these compounds is remarkable when compared to their five-coordinate precursors. For example, PCl_5 or even RPCl_4 readily undergoes fluorination, silylation, and alkylation.

To understand this lack of reactivity one must rationalize the reaction mechanisms involved. Similar to the more widely studied carbon compounds, four-coordinate phosphorus(V) (e.g. $\text{Cl}_3\text{P}(\text{O})$, PCl_4^+ , PO_4^{3-}) may undergo $\text{S}_\text{N}1$ or $\text{S}_\text{N}2$ reaction mechanisms (eq.(11a) and (11b)) to form another λ^4 -phosphorus compounds in nucleophilic substitutions.

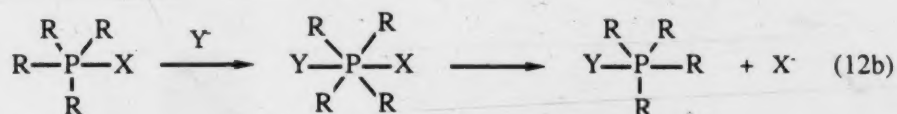


However, the trigonal bipyramidal phosphorus intermediate has a finite existence ($>>10^{-13}$ s) unlike the analogous $\text{S}_\text{N}2$ carbon intermediates, which are more transitory ($\sim 10^{-13}$ s).²⁰ In some cases, these phosphorus $\text{S}_\text{N}2$ intermediates can be observed and even isolated. The stability of this five-coordinate intermediate and hence the $\text{S}_\text{N}2$ mechanism is determined by:

- (1) the ability of the substituents to act as good leaving groups and
- (2) the steric hindrance around phosphorus.

If the substituents are bulky and are good leaving groups, an S_N1 mechanism is preferred (eq.(11a)). Conversely, if the substituents are not good leaving groups and are not too bulky to allow pentacoordination, an S_N2 mechanism is preferred (eq.(11b)).

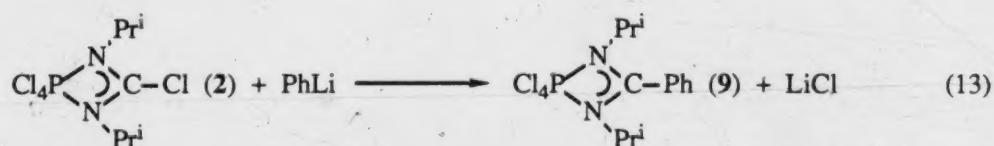
Nucleophilic substitution reactions of pentacoordinate phosphorus have no direct parallels in carbon chemistry, but there is some evidence that they can also proceed via an S_N1 or S_N2 mechanism (eqs. (12a) and (12b)).²⁵



Again, both the ability of the substituents on phosphorus to act as good leaving groups and the steric hindrance around phosphorus will determine whether the mechanism is S_N1 or S_N2 .

The nucleophilic substitution reaction at a hexacoordinate phosphorus center must proceed by way of an S_N1 mechanism. No evidence of a λ^7 -phosphorus compound or intermediate species has ever been reported and so the occurrence of an S_N2 mechanism is very unlikely. In the S_N1 mechanism there must be a leaving group to form a λ^5 -phosphorus intermediate to allow nucleophilic substitution. For **2** this would involve either a ring opening or a removal of a chlorine atom to form the λ^5 -phosphorus intermediates $Cl_4P-(DPC)Cl$ or $Cl_3P(DPC)Cl^+ Cl^-$, respectively. The resistance of **2** to simple nucleophilic substitution, coupled with multinuclear NMR evidence showing no fluxional behaviour (in compounds **3** to **8**) indicates that no such five-coordinate intermediate exists. This implies that the four-membered chelate formed in these molecules is very stable to ring opening, and the P-Cl bond is less reactive than expected.

Under vigorous conditions, fluorine can be substituted for chlorine in a metathesis reaction with AgF, giving a mixture of **2**, $\text{Cl}_3\text{FP}(\text{DPC})\text{Cl}$, and $\text{Cl}_2\text{F}_2\text{P}(\text{DPC})\text{Cl}$. The use of other fluorinating agents, such as NaF, generated the completely fluorinated anion PF_6^- with no evidence of any intermediate species. The use of the strong arylating agent, phenyllithium, led to substitution of the chlorine on the ring and not of the chlorines on phosphorus (Figure 3.8 and eq.(13)).



Compound **9** has been characterized by ^{31}P and ^1H -NMR spectroscopy (Table 3.6 and detailed in Results and Discussion 3.3.3), infrared spectroscopy (Table 3.7 and 3.8), mass spectroscopy and elemental analysis (Experimental 3.2.10). Substitution of the phenyl group in **9** at the ring carbon instead of the phosphorus and the fluorination (by metathesis) at the phosphorus center under vigorous conditions, again illustrate the inertness of the P-Cl bonds in **2**.

It seems that these hexacoordinate phosphoranes are reactively inert for two reasons: they lack a good leaving group, and they are coordinatively saturated and unable to form λ^7 -phosphorus intermediates. This resistance to nucleophilic substitution is not limited to the series of λ^6 -(carbodiimide)phosphoranes, but has also been observed in other hexacoordinate phosphorus compounds such as the λ^6 -(pyrindinol)phosphoranes presented in Chapter 4.

3.4 Conclusion

This chapter described the preparation and characterization of a series of neutral hexacoordinate phosphorus compounds (1-8) containing a strained four-membered ring. These compounds all possess a low-frequency shift in their ^{31}P NMR spectra.

The X-ray crystal structure of $\text{Cl}_2(\text{CF}_3)_2\text{P}(\text{DCC})\text{Cl}$ (5) shows a six-coordinate environment around phosphorus with two axial CF_3 groups mutually trans to each other and orthogonal to the plane of the chelating ring (Figure 3.2). Although the crystal was severely disordered, the analysis of the solid-state structure of $\text{Cl}(\text{CF}_3)_3\text{P}(\text{DCC})\text{Cl}$ (7) indicates a distorted octahedral geometry around phosphorus with two axial CF_3 groups and one radial CF_3 group. Both these stereochemistries are in accord with multinuclear NMR results.

Finally, in order to explore the chemistry of neutral hexacoordinate phosphorus compounds, a reactivity study was carried out using $\text{Cl}_4\text{P}(\text{DPC})\text{Cl}$ (2). This is the first such investigation reported for any neutral hexacoordinate phosphorus compound. It was discovered that, apart from readily hydrolyzing to form $\text{Cl}_2(\text{O})\text{P}(\text{DPC})\text{Cl}$ (10), 2 was surprisingly resistant to simple nucleophilic substitutions (Figure 3.8), implying a very inert P-Cl bond compared to the P-Cl bonds in analogous five-coordinate compounds, such as PCl_5 and PhPCl_4 . Reacting phenyllithium with 2 resulted in substitution of chlorine on the chelating ring (not the phosphorus), which further displayed the inertness of the P-Cl bond in this hexacoordinate phosphorus compound.

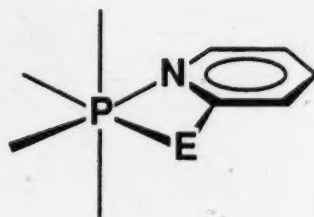
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Bennett, F.W.; Emeleus, H.J.; Haszeldine, R.N.; *J. Chem. Soc.*, 1953, 1565.
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- 6 *International Tables for X-Ray Crystallography* (1974). Vol. IV. Table 2.2B. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
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CHAPTER IV

PYRIDINOL DERIVATIVES OF HEXACOORDINATE PHOSPHORUS(V)



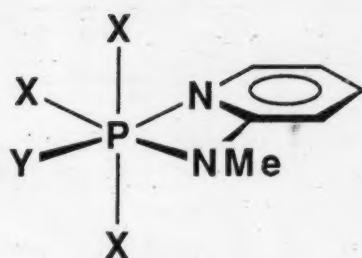
4.1 Introduction

Chapters 2 and 3 described series of λ^6 -phosphoranes containing various substituents (F, Cl, CF_3 , and CH_3) attached to the central phosphorus atom. This chapter describes a series of pyridine-based chelating ligands, namely 2-(methylamino)pyridine, 2-hydroxypyridine, 2-mercaptopyridine, and 2, 2'-dipyridylamine, which have been used to generate a series of neutral hexacoordinate phosphorus compounds (1-8, Figure 4.1). These ligands form strained four-membered rings with phosphorus similar to those discussed in Chapter 3. The object in this chapter is to study the effects of variations (e.g. changing chelating atoms O, S, N) of the character of the bidentate chelating ligand, while keeping the phosphorus substituent environment constant. Such modifications of pyridine-based ligands can be used to investigate trends in behaviour, such as deshielding of the phosphorus center or fluxionality in NMR spectroscopy. In addition, these ligands are unsymmetrical and, like the aminoacac ligands of Chapter 2, this feature facilitates spectroscopic characterization. The synthesis and characterization of these compounds (1-8) by X-ray crystallography and by multinuclear NMR and mass spectroscopies is reported.

4.2 Experimental

4.2.1 General Procedures

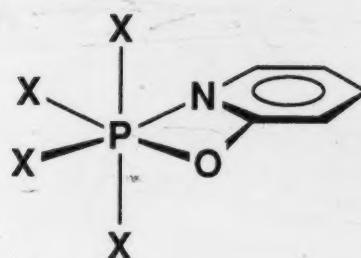
The trifluoromethyl phosphorane $(\text{CF}_3)_3\text{PCl}_2$ was prepared according to published methods.¹ The reactants PF_5 , PCl_5 , 2-(methylamino)pyridine, 2-hydroxypyridine, 2-mercaptopyridine and 2, 2'-dipyridylamine were obtained from Aldrich and used without further purification. All solvents were dried and distilled before use. The ^1H , ^{19}F , and ^{31}P NMR spectra were obtained using Bruker WP200, WP80, and WP400 spectrometers.



1 $X = Y = \text{Cl}$

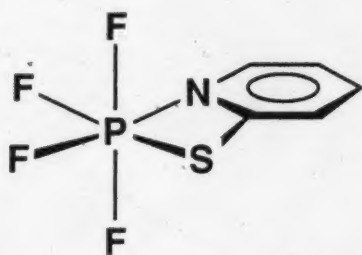
2 $X = Y = \text{F}$

6 $X = \text{CF}_3, Y = \text{Cl}$

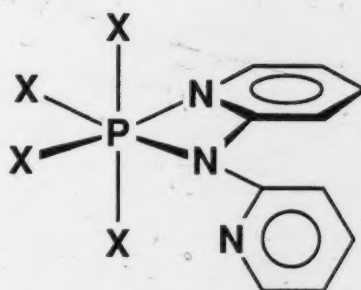


3 $X = \text{Cl}$

4 $X = \text{F}$



5



7 $X = \text{Cl}$

8 $X = \text{F}$

Figure 4.1 Pyridine-based λ^6 -phosphorus compounds (1-8).

Samples were recorded as CDCl_3 solutions (approximately 10% compound) in vacuum sealed 5mm NMR tubes. Mass spectra were recorded with an AEI MS-12 spectrometer operating at an ionizing voltage of 70 eV. All manipulations were carried out either in vacuum or under dry argon.

4.2.2 Preparation of the silylated pyridine ligands

A general synthesis of these silylated pyridine ligands is given below, and the details of each preparation are listed in Table 4.1.

A weighed sample of the pyridinol ligand was placed in a 500 mL round bottom flask and dissolved in 200 mL of diethyl ether. The solution was stirred and cooled in an ice bath. A diethyl ether solution of CH_3Li (1.4 M) was added dropwise over a period of one hour. The solution was warmed to room temperature for two hours and then cooled again in an ice bath. An equivalent amount of $(\text{CH}_3)_3\text{SiCl}$ was added dropwise for one half hour. The solution was warmed to room temperature and left to stir for an additional three hours. The white precipitate which formed was filtered using a C glass frit and the diethyl ether was removed using a rotary evaporator. Distillation of the remaining liquid (solid with the 2, 2'-dipyridyltrimethylsilylamine preparation) using a 15 cm, vacuum jacketed, Vigreux column afforded pure product (yields are given in Table 4.1) which was analyzed by ^1H NMR spectroscopy (Table 4.2).

4.2.3 Preparation of 2-(methylamino)pyridinetetrachloro-phosphorus(V) (1)

A sample of 2-(trimethylsilylmethylamino)pyridine (1.40 g, 7.79 mmol) was placed in a round bottom flask and dissolved in CCl_4 . An equivalent amount of PCl_5 (1.61 g, 7.74 mmol) was dissolved in CCl_4 and this PCl_5 solution was added directly to the 2-(trimethylsilylmethylamino)pyridine solution at room temperature. A yellow precipitate

Table 4.1 Details of Silylated Pyridine Ligand Preparations

Compound	Acid ^a wt (g)	CH ₃ Li (1.4 M) vol (mL)	(CH ₃) ₃ SiCl wt (g)	Yield %	mp/bp ^b (deg)
Me ₃ Si(map)	8.12	56.4	8.79	76	bp 103
Me ₃ Si(hp)	6.54	50.6	8.08	92	bp 97
Me ₃ Si(mp)	7.23	48.9	7.57	68	bp 122
Me ₃ Si(dpa)	9.45	41.1	6.36	83	mp 37-40

Table 4.2 The ¹H NMR chemical shifts^c for silylated pyridine ligands.

	Me ₃ Si(map) ^d	Me ₃ Si(hp) ^e	Me ₃ Si(mp) ^d	Me ₃ Si(dpa) ^e
(CH ₃) ₃ Si	0.045 s	0.30 s	0.21 s	0.25 s
	6.55 d	7.00-7.25 m	6.94 br tr	6.55 d
Pyridine Ring Protons	6.66 d/d	—	7.26 d	6.86 br tr
	7.53 d/tr	7.80 br tr	7.41 br tr	7.54 d/tr
	8.21 d/d	8.45 br d	8.30 br s	8.41 br d

^a Protonated form of the pyridine ligand.

^b Boiling points at 0.5 mmHg.

^c Chemical shifts in ppm vs TMS.

^d 400 MHz instrument used.

^e 80 MHz instrument used.

Abbreviations:

s = singlet
d = doublet
tr = triplet
m = multiplet
br = broad

map = 2-(methylamino)pyridine
hp = 2-hydroxypyridine
mp = 2-mercaptopyridine
dpa = 2, 2'-dipyridylamine

formed immediately, however, the solution was stirred under Ar for several hours to ensure complete reaction. The solvent was removed under vacuum, to leave a yellow solid (mp 167-172° C).

Anal. for $C_6H_7Cl_4N_2P$:

Calcd.: C, 25.74; H, 2.52; Cl, 50.66; N, 10.01

Found: C, 25.57; H, 2.39; Cl, 48.35; N, 9.92 %.

MS: m/e (Rel. int., % of strongest peak) identity: 280 (7.5) M; 243 (100) M - Cl; 208 (41.9) M - 2Cl; 173 (54.1) PCl_4 ; 137 (5.3) PCl_3 ; 107 (92.9) $NC_5H_4NCH_3$; 78 (11.3) NC_5H_4 .

4.2.4 Preparation of 2-(methylamino)pyridinetetrafluoro-phosphorus(V) (2)

A sample of 2-(trimethylsilylmethylamino)pyridine (0.637 g, 3.54 mmol) was placed in a small glass reaction vessel and degassed three times using a freeze-thaw cycle. Then 3 mL of $CFCl_3$ was cryogenically distilled in, followed by a sample of PF_5 (360 mmHg, 183 mL, 3.55 mmol). The vessel was flame sealed under vacuum and allowed to warm to room temperature for three hours to form a white precipitate. The glass reaction vessel was opened under vacuum with a Stock-breaker and the volatile materials were pumped away, to leave a white solid (mp 105-108° C).

Anal. for $C_6H_7F_4N_2P$:

Calcd.: C, 33.66; H, 3.30; N, 13.08

Found: C, 33.34; H, 3.46; N, 12.70

MS: m/e (Rel. int., % of strongest peak) identity: 214 (24.1) M; 195 (16.8) M - F; 107 (100) PF_4 ; 92 (2.1) NC_5H_4N ; 79 (22.6) NC_5H_4 .

4.2.5 Preparation of tetrachloro-2-hydroxypyridine-phosphorus(V) (3)

A sample of 2-(trimethylsilylhydroxy)pyridine (1.78 g, 10.65 mmol) was placed in a round bottom flask and mixed with 50 mL of CCl_4 . An equivalent amount of PCl_5 (2.21 g, 10.61 mmol) was dissolved in 50 mL of CCl_4 and this solution was added directly to the 2-(trimethylsilylhydroxy)pyridine. A white precipitate formed immediately, however, the solution was stirred under Ar for several hours to ensure complete reaction. The solvent was removed under vacuum, to leave a white solid (mp 123-125° C).

Anal. for $\text{C}_5\text{H}_4\text{Cl}_4\text{NOP}$:

Calcd.: C, 22.50; H, 1.51; Cl, 53.14; N, 5.25

Found: C, 24.37; H, 1.85; Cl, 48.01; N, 5.62 %.

MS: m/e (Rel. int., % of strongest peak) identity: 232 (21.2) M - Cl; 173 (19.3) PCl_4 ; 160 (20.2) M - 3Cl; 101 (10.7) PCl_2 ; 78 (100) NC_5H_4 ; 66 (96) PCl.

4.2.6 Preparation of tetrafluoro-2-hydroxypyridine-phosphorus(V) (4)

A sample of 2-(trimethylsilylhydroxy)pyridine (0.999 g, 5.98 mmol) was placed in a small glass reaction vessel and degassed three times using a freeze-thaw cycle. Then 5 mL of CFCl_3 was cryogenically distilled in, followed by a sample of PF_5 (608 mmHg, 183 mL, 5.98 mmol). The vessel was flame sealed under vacuum and allowed to warm slowly to room temperature for three hours to form a white precipitate. The glass reaction vessel was opened under vacuum with a Stock-breaker and the volatiles were pumped away, to leave a white solid (mp 83-85° C).

Anal. for $\text{C}_5\text{H}_4\text{F}_4\text{NOP}$:

Calcd.: C, 29.87; H, 2.01; N, 6.97

Found: C, 29.67; H, 1.96; N, 6.86 %.

MS: m/e (Rel. int., % of strongest peak) identity: 201 (16.7) M; 182 (1.4) M - F; 107 (100) PF₄; 95 (16.6) NC₅H₄O; 78 (13.3) NC₅H₄, 64 (11.2) C₅H₄.

4.2.7 Preparation of tetrafluoro-2-mercaptopyridine (5)

A sample of 2-(trimethylsilylmercapto)pyridine (0.57 g, 3.1 mmol) was placed in a small glass reaction vessel and degassed three times using a freeze-thaw cycle. Then a sample of PF₅ (318 mmHg, 183 mL, 3.13 mmol) was cryogenically distilled into the vessel with no solvent. The vessel was flame sealed under vacuum and allowed to warm slowly to room temperature for three hours to form a light yellow precipitate. The glass reaction vessel was opened under vacuum with a Stock breaker and the volatiles were pumped away, to leave a yellow solid (mp 95-99° C).

Anal. for C₅H₄F₄NPS:

Calcd.: C, 23.24; H, 1.97; N, 6.83

Found: C, 23.42; H, 1.72; N, 6.80 %.

MS: m/e (Rel. int., % of strongest peak) identity: 187 (17.0) M - F; 142 (6.3) NC₅H₄SP; 107 (100) PF₄; 78 (41.6) NC₅H₄, 67 (15.1) PF₂.

4.2.8 Preparation of chloro(2-mercaptopyridine)tris(trifluoromethyl)-phosphorus(V) (6)

A sample of 2-(trimethylsilylmethylamino)pyridine (0.064 g, 0.35 mmol) was placed in a small glass reaction vessel and degassed three times using a freeze-thaw cycle. Then 2 mL of CFCl₃ was distilled in, followed by a sample of (CF₃)₃PCl₂ (0.0949 g, 0.307 mmol). The vessel was flame sealed under vacuum and allowed to warm slowly to room temperature for three hours to form a white precipitate. The glass reaction vessel was opened under vacuum with a Stock-breaker and the volatiles were pumped away, to leave a white solid (mp 105-108° C).

Anal. for $C_6H_7F_4N_2P$:

Calcd.: C, 28.40; H, 1.85; N, 7.36

Found: C, 29.97; H, 2.04; N, 7.56 %.

MS: m/e (Rel. int., % of strongest peak) identity: 380 (3.7) M; 365 (10.4) M-CH₃; 345 (41.5) M-Cl; 311 (100) M-CF₃; 295 (11.3) CF₃ClPNC₅H₄N; 273 (6.0) C₃F₉ClP; 261 (25.7) C₂F₆PNC₅H₄N; 228 (12.9) CF₃ClPNC₅H₄N; 137 (17.7) PNC₅H₄NCH₃; 107 (19.5) NC₅H₄NCH₃; 78 (72.2) NC₅H₄; 69 (38.8) CF₃.

4.2.9 Preparation of (2, 2'-dipyridylamino)tetrachloro-phosphorus(V) (7)

A sample of 2, 2'-dipyridyltrimethylsilylamine (0.83 g, 4.8 mmol) was placed in a round bottom flask and mixed with 50 mL of CCl₄. An equivalent amount of PCl₅ (1.00 g, 4.80 mmol) was dissolved in 50 mL of CCl₄ and this solution was added directly to the 2, 2'-dipyridyl-trimethylsilylamine solution at room temperature. A yellow precipitate formed and the solution was stirred under Ar for several hours to ensure complete reaction. The solvent was removed under vacuum, to leave a yellow solid (mp 163-166° C).

Anal. for $C_{10}H_8Cl_4N_3P$:

Calcd.: C, 34.82; H, 2.92; Cl, 41.10; N, 12.18

Found: C, 35.10; H, 2.62; Cl, 39.63; N, 12.22 %.

MS: m/e (Rel. int., % of strongest peak) identity: 306 (12.6) M - Cl; 271 (9.0) M - 2Cl; 236 (72.2) M - 3Cl; 200 (14.4) M - 4Cl; 170 (100) NC₁₀H₈N₂; 122 (43.3) PNC₅H₄N; 101 (41.7) PCl₂; 78 (77.7) NC₅H₄.

4.2.10 Preparation of (2, 2'-dipyridyltrimethylsilylamine)tetrafluoro-phosphorus(V) (8)

A sample of 2, 2'-dipyridyltrimethylsilylamine (0.386 g, 1.60 mmol) was placed in a small glass reaction vessel which was then evacuated. Then 4 mL of CFC_3 was distilled in, followed by a sample of PF_5 (163 mmHg, 183 mL, 1.60 mmol). The vessel was flame sealed under vacuum and allowed to warm slowly to room temperature for three hours to form a white precipitate. The glass reaction vessel was opened under vacuum with a Stock-breaker and the volatiles were pumped away, to leave a white solid (mp 77-79° C).

Anal. for $\text{C}_{10}\text{H}_8\text{F}_4\text{N}_3\text{P}$:

Calcd.: C, 43.34; H, 2.91; N, 15.16

Found: C, 41.92; H, 2.89; N, 14.61 %.

MS: m/e (Rel. int., % of strongest peak) identity: 277 (100) M; 258 (8.6) M - F; 170 (90.4) $\text{NC}_{10}\text{H}_8\text{N}_2$; 107 (79.2) PF_4 ; 92 (2.5) $\text{NC}_5\text{H}_4\text{N}$; 78 (50.8) NC_5H_4 ; 51 (18.7) PF.

4.2.11 X-ray Data Collection²

A yellow crystal of $\text{C}_6\text{H}_7\text{Cl}_4\text{N}_2\text{P}$ (1), having an irregular shape with the approximate dimensions of 0.10 x 0.35 x 0.36 mm, was mounted in a capillary under a nitrogen atmosphere, and optically centered in the X-ray beam of an Enraf-Nonius CAD4 automated diffractometer. Data collection and refinement was carried out by Professor A.A. Pinkerton of the University of Toledo. All intensity measurements were performed using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite crystal, incident beam monochromator (Table 4.3).

Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 10 reflections in the range $10 < \pm < 12^\circ$, measured by the computer controlled diagonal slit method of centering. The orthorhombic cell parameters and calculated volume are: $a = 7.507(3)$, $b = 11.623(3)$,

Table 4.3 Crystal Data and Details of Intensity Collection

Cl ₄ P(2-methylaminopyridine) (1)	
mol formula	C ₆ H ₇ Cl ₄ N ₂ P
fw	279.92
cryst size (mm)	0.10 x 0.35 x 0.36
systematic absences	<i>h</i> 00 (<i>h</i> odd), 0 <i>k</i> 0 (<i>k</i> odd), 00 <i>l</i> (<i>l</i> odd)
space group	orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
temp (°C)	-20(1)
radiation (λ, Å)	Mo Kα (0.71073)
unit cell parameters	
<i>a</i> (Å)	7.507 (3)
<i>b</i> (Å)	11.623 (3)
<i>c</i> (Å)	12.577 (2)
Volume (Å ³)	1097.4
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.69
linear abs coeff μ (cm ⁻¹)	11.9
max 2θ reflections	
collected (deg)	52.0
takeoff angle (deg)	2.8
detector aperture (mm)	2.0 to 2.1(horiz), 4.0 (vert)
cryst to detector dist (mm)	210
scan type	ω-θ
scan rate (deg min ⁻¹)	1 to 7 (in omega)
scan width (deg)	0.70 + 0.34 tanθ
total reflections collected	1275
no. of observs (<i>I</i> > 3σ(<i>I</i>))	843
no. of variables	134
final R, R _w , GOF ^a	0.038, 0.045, 1.47

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2};$$

$$GOF = [\sum w(|F_o| - |F_c|)^2 / (NO - NV)]^{1/2}$$

$c = 12.577(2) \text{ \AA}$, $V = 1097.4 \text{ \AA}^3$. For $Z = 4$ and $F.W. = 279.92$ the calculated density is 1.69 g/cm^3 . As a check on crystal quality, omega scans of several intense reflections were measured; the width at half-height was 0.17° with a take-off angle of 2.8° , indicating good crystal quality. The automatic peak search and reflection indexing programs³ generated a preliminary orthorhombic unit cell, and the systematic absences of $h00$, (h odd), $0k0$, (k odd), and $00l$, (l odd) led to the space group $P2_12_12_1$ (No. 19).⁴

The intensity data were collected at -20°C using a $\omega - 2\theta$ scan of variable speed, 1 to 7 deg min^{-1} in θ . The scan range varied as a function of θ to compensate for $\alpha_1 - \alpha_2$ wavelength dispersion: omega scan width = $0.70 + 0.34 \tan(\theta)^\circ$. Backgrounds for the peaks were measured by extending the scan 25% on each side; this gave a peak-to-background counting time ratio of 2:1. Intensity measurements were made out to a maximum 2θ of 52° . The counter aperture was also adjusted as a function of θ . The horizontal aperture width ranged from 2.0 to 2.1 mm; the vertical aperture was set at 4.0 mm. The diameter of the incident beam collimator was 0.8 mm and the crystal to detector distance was 21 cm. For intense reflections an attenuator was automatically inserted in front of the detector; the attenuator factor was 13.5.

4.2.12 X-ray Data Reduction

A total of 1275 reflections were collected, of which 1275 were unique. As a check on crystal and electronic stability 3 representative reflections were measured every 50 minutes. The slope of the least-squares line through a plot of intensity versus time corresponds to a total loss in intensity of 0.5%. An anisotropic decay correction was applied. The correction factors on I ranged from 0.967 to 1.049 with an average value of 1.001.

Lorentz and polarization factors were applied: $I = r(S - 2B)/L_p$; $\sigma(I) = [r(S + 4B) + (0.040/I)^2]^{1/2}/L_p$, where r is the scan rate, S is the total scan count, B is the total background count, and L_p is the combined Lorentz and polarization factor. The linear absorption coefficient is 11.9 cm^{-1} for Mo $K\alpha$ radiation. An empirical absorption correction based on a series of psi-scans was applied to the data. Relative transmission coefficients ranged from 0.834 to 0.995 with an average value of 0.941.

4.2.13 Structure Solution and Refinement

The structure was solved by direct methods. Using 166 reflections (minimum E of 1.53) and 2161 relationships, a total of 13 phase sets were produced. A total of 5 atoms were located from an E-map prepared from the phase set with probability statistics: absolute figure of merit = 1.12, residual = 7.91, and psi zero = 2.502. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement, but three of them were restrained to ride on the atom to which they were bonded. Adjustment of atomic parameters was carried out by full-matrix least-squares refinement on F_o minimizing the function $\sum w (|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes and the weight w is given by $w = 4F_o^2 / \sigma^2(F_o^2)$.

Scattering factors were taken from Cromer and Waber.⁵ Anomalous dispersion effects were included in F_c ;⁶ the values for f' and f'' were those of Cromer.⁷ After rejecting the systematically absent reflections there were 843 reflections with $I > 3\sigma(I)$, which were used in the subsequent refinement. In the final cycle 134 parameters were refined using 843 observations with $I > 3\sigma(I)$ with the largest and average shift/error less than 0.1. As a result, the goodness-of-fit was 1.47, and $R = \sum ||F_o| - |F_c|| / \sum |F_c| = 0.038$ and $R_w = (\sum w (|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2} = 0.045$. There was one correlation coefficient

greater than 0.50. The highest correlation coefficient was 0.58 between parameters 19 and 28. The highest peak in the final difference Fourier map has a density of $0.42(8) \text{ e } \text{\AA}^{-3}$. An analysis of R_w in terms of F_o , $\sin \theta / \lambda$, and various combinations of Miller indices indicated no unusual trends. All calculations were performed on a VAX11/750 computer using SDP/VAX.⁸

The positional and isotropic thermal parameters for compound 1 are given in Table 4.4. Bond lengths and angles are given in Tables 4.5 and 4.6. Additional information is available in the report provided by Dr. A.A. Pinkerton, University of Toledo, Toledo, Ohio, U.S.A. (Ref.No. FRAPPI04).

4.2.14 Calculation of the Energy Barrier of Fluorine Exchange in 2

Free energy of activation ($\Delta G^\ddagger$) for the fluorine exchange in 2 was determined by means of an NMR double resonance technique known as spin saturation transfer (SST). The experiment was carried out on a Bruker WP400 spectrometer at 243K (-30° C). The axial fluorines were saturated at -69.9 ppm, causing partial saturation of the radial fluorines. The spin-lattice relaxation times (T_1) of the radial fluorines were determined by standard literature methods.⁹ The two rate constants for two site axial-radial fluorine exchange at -30° C were calculated using equation (1), where M_z^∞ is the equilibrium magnetization with saturation at another site, and M_z^0 is the normal magnetization without saturation.

$$k = \frac{1}{T_1} \left[\frac{M_z^0 - M_z^\infty}{M_z^\infty} \right] \quad (1)$$

An average rate constant was derived from the two individual rate constants. Once the average rate constant (k) had been calculated, equation (2), where R is the gas constant, T

Table 4.4 Positional^a and Thermal Parameters for Cl₄P(2-methylaminopyridine) (1)

atom	x	y	z	B, ^b Å ²
P	4768 (2)	546 (1)	1011 (1)	2.70 (3)
Cl(1)	1901 (2)	521 (1)	962 (2)	4.76 (4)
Cl(2)	7611 (2)	499 (2)	1110 (2)	5.56 (5)
Cl(3)	4770 (2)	2324 (1)	1172 (1)	4.19 (3)
Cl(4)	4628 (4)	139 (1)	2638 (1)	5.41 (5)
N(1)	4784 (6)	-970 (3)	574 (3)	2.49 (9)
N(2)	4841 (8)	497 (4)	-390 (3)	3.4 (1)
C(1)	4829 (8)	-657 (4)	-459 (4)	2.7 (1)
C(2)	4850 (9)	-1490 (5)	-1249 (4)	3.7 (1)
C(3)	4779 (9)	-2608 (5)	-917 (4)	4.1 (1)
C(4)	4720 (10)	-2909 (4)	140 (5)	4.0 (1)
C(5)	4719 (8)	-2072 (4)	892 (4)	3.4 (1)
C(6)	4880 (10)	1319 (5)	-1236 (5)	4.8 (2)
H(2)	4670 (70)	-1260 (40)	-1960 (40)	4 (1) ^c
H(3)	4770 (70)	-3120 (50)	-1460 (40)	4 (1) ^c
H(4)	4660 (80)	-3710 (50)	370 (50)	6 (2) ^c
H(5)	4720 (60)	2190 (40)	1620 (30)	2 (1) ^c
H(6A)	4920	930	-1900	6.4 ^d
H(6B)	3840	1780	-1200	6.4 ^d
H(6C)	5900	1790	-116	6.4 ^d

^a Values $\times 10^4$.

^b Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

^c This atom was refined isotropically.

^d This atom was not refined.

Table 4.5 Bond Distances^a for Cl₄P(2-methylaminopyridine) (1)

atom 1	atom 2	dist	atom 1	atom 2	dist
P	Cl(1)	2.153 (2) ^b	C(2)	C(3)	1.366 (8)
P	Cl(2)	2.139 (2)	C(2)	H(2)	0.94 (5)
P	Cl(3)	2.077 (2)	C(3)	C(4)	1.375 (8)
P	Cl(4)	2.103 (2)	C(3)	H(3)	0.91 (5)
P	N(1)	1.845 (4)	C(4)	C(5)	1.357 (7)
P	N(2)	1.763 (4)	C(4)	H(4)	0.97 (6)
N(1)	C(1)	1.350 (6)	C(5)	H(5)	0.92 (2)
N(1)	C(5)	1.343 (6)	C(6)	H(6A)	0.950
N(2)	C(1)	1.344 (6)	C(6)	H(6B)	0.950
N(2)	C(6)	1.430 (7)	C(6)	H(6C)	0.950
C(1)	C(2)	1.388 (7)			

^a In angstroms.^b Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 4.6 Bond Angles^a for Cl₄P(2-methylaminopyridine) (1)

atom 1	atom 2	atom 3	angle
Cl(1)	P	Cl(2)	177.2 (1) ^b
Cl(1)	P	Cl(3)	90.96 (9)
Cl(1)	P	Cl(4)	88.6 (1)
Cl(1)	P	N(1)	89.2 (2)
Cl(1)	P	N(2)	90.2 (2)
Cl(2)	P	Cl(3)	91.07 (9)
Cl(2)	P	Cl(4)	89.3 (1)
Cl(2)	P	N(1)	89.2 (2)
Cl(2)	P	N(2)	91.5 (2)
Cl(3)	P	Cl(4)	97.39 (9)
Cl(3)	P	N(1)	168.3 (2)
Cl(3)	P	N(2)	97.4 (2)
Cl(4)	P	N(1)	94.3 (1)
Cl(4)	P	N(2)	165.2 (2)
N(1)	P	N(2)	70.9 (2)
P	N(1)	C(1)	91.7 (2)
P	N(1)	C(5)	145.2 (4)
C(1)	N(1)	C(5)	123.0 (4)
P	N(2)	C(1)	95.5 (3)
P	N(2)	C(6)	136.3 (4)
C(1)	N(2)	C(6)	128.2 (4)
N(1)	C(1)	N(2)	101.9 (4)
N(1)	C(1)	C(2)	120.1 (4)
N(2)	C(1)	C(2)	137.9 (5)
C(1)	C(2)	C(3)	116.4 (5)
C(1)	C(2)	H(2)	118 (3)
C(3)	C(2)	H(2)	124 (3)
C(2)	C(3)	C(4)	122.6 (5)
C(2)	C(3)	H(3)	114 (3)
C(4)	C(3)	H(3)	124 (3)
C(3)	C(4)	C(5)	119.4 (5)
C(3)	C(4)	H(4)	122 (3)
C(5)	C(4)	H(4)	119 (3)
N(1)	C(5)	C(4)	118.4 (5)
N(1)	C(5)	H(5)	116 (3)
C(4)	C(5)	H(5)	125 (3)
N(2)	C(6)	H(6A)	110.0
N(2)	C(6)	H(6B)	109.2
N(2)	C(6)	H(6C)	109.2
H(6A)	C(6)	H(6B)	109.5
H(6A)	C(6)	H(6C)	109.5
H(6B)	C(6)	H(6C)	109.5

^a In degrees.^b Numbers in parantheses are estimated standard deviations in the least significant digits.

is the temperature, N is Avogadro's number, and h is Planck's constant, could be used to determine the free energy of activation ($\Delta G^\ddagger$) of the fluorine exchange in **2**.

$$\Delta G^\ddagger = -RT \ln k \left(\frac{N h}{R T} \right) \quad (2)$$

The energy barrier to fluorine exchange in compound **2**, based on average two-site exchange, was calculated to be 56.4(5) kJ/mol at -30° C.

In addition, another magnetization transfer experiment known as selective inversion transfer was carried out to determine a more reliable $\Delta G^\ddagger$ value. In this experiment a selective inversion of the upfield radial fluorine (F_{rad}) at -89.0 ppm is applied and the temporal response of the z-magnetizations (M_z) at the other two sites (F_{ax} and F_{rad}) are then observed during an evolution period. The pulse sequence:

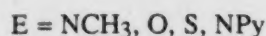
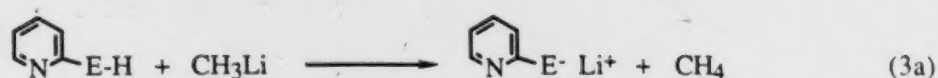
Relaxation	—	Selective	—	τ	—	Non selective	—	Aquisition
Delay		180° Pulse				90° Pulse		

is repeated for a series of τ values, where $0 \leq \tau \leq 5T_1$. The experiment was carried out on a Bruker WP400 spectrometer at 243K (-30° C). The resulting magnetizations are listed in Table 4.8. Using a computer program developed by Muhandiram and McClung¹⁰ the data was determined to best fit a mixture of two exchange mechanisms possessing rate constants k_1 and k_2 for pseudorotation fluorine exchange and radial fluorine exchange, respectively. The two energy barriers to fluorine exchange in compound **2** were calculated using equation (2). The energy barriers for pseudorotation fluorine exchange ($\Delta G_1^\ddagger$) and radial fluorine exchange ($\Delta G_2^\ddagger$) were determined to be 57.8(1) and 56.1(1) kJ/mol at -30° C.

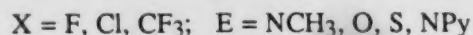
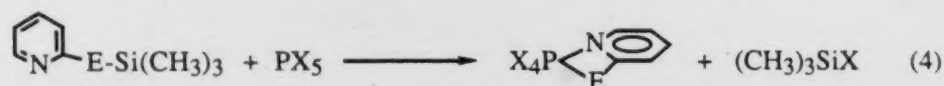
4.3 Results and Discussion

Although bidentate heteroatomic pyridine-based ligands have seen limited use for the preparation of metal chelates (e.g. 2-aminopyridine to form $[\text{H}(\text{Ph}_3\text{P})_2\text{Ru}(\text{HNC}_5\text{H}_4\text{N})]$, 2-mercaptopyridine to form $[(\text{Ph}_3\text{P})_2\text{Ru}(\text{SC}_5\text{H}_4\text{N})_2]$,¹¹ and 2-hydroxypyridine to form several bimetallic compounds of the type $[\text{M}_2(6\text{-methyl-2-hydroxypyridine})_4]$ ¹² where $\text{M} = \text{Mo}, \text{Ru}, \text{Rh}, \text{Pd}, \text{Cr}$) this ligand system has not been extended to main group elements. The 8-hydroxyquinoline ligand, which is chemically similar to 2-hydroxypyridine ligand, has been used to chelate phosphorus forming a five-membered ring. However, the novel feature displayed in the present cases is the formation of the potentially more strained four-membered ring. It might be expected that formation of a λ^5 -phosphorus compound with no ring structure, or polymerization of the compound, would be favoured over the chelation that is actually observed. For example, with metals, 2-hydroxypyridine does not normally act as a bidentate ligand, but usually serves to bridge dinuclear species or polymeric species. (Some exceptions, such as *trans*- $[\text{Ru}(6\text{-methyl-2-hydroxypyridine})_2(\text{PPh}_3)_2]$ ¹³, are known.) Chelation of phosphorus using such small-bite ligands has already been shown in a few examples of carbamates, benzamidines, and carbodiimides (Chapter 3).

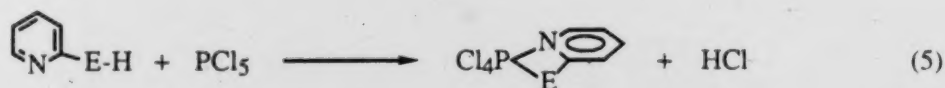
The title compounds (1-8) are all readily prepared using the silylated pyridine derivative. The silylated derivative can be prepared as shown in eqs. (3a) and (3b) from the protonated form of the ligand, which is commercially available.



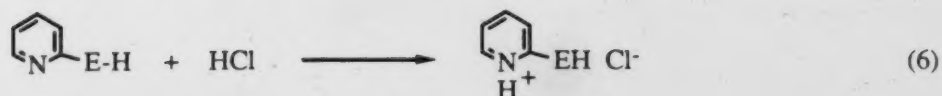
Reacting these silylated derivatives with a λ^5 -phosphorane gives high yields of the λ^6 -phosphoranes with elimination of $(\text{CH}_3)_3\text{SiCl}$ or $(\text{CH}_3)_3\text{SiF}$ as shown in equation (4).



The chloro analogues (1, 3, 6, and 7) can also be prepared from the protonated form of the ligand. In these cases refluxing in CCl_4 is required to eliminate HCl as shown in equation (5).



However, this method is time-consuming and not as clean as the preparation using the silylated ligands, which gives typical yields of 80-90%. The HCl generated by initial displacement is in competition with PCl_5 to form various by-products, which lowers the yield of the desired λ^6 -phosphorus product. The nitrogen of the pyridine ring (in 1, 3, 6, 7) and the nitrogen of the amino group (in 1, 6, 7) reacts with HCl to form stable ammonium chloride salts in the reaction mixture (eqs. (6) and (7)).



Similar complicating problems of ammonium chloride salt formation have been encountered in preparations of $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{aminoacac})$ and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{methylaminoacac})$ discussed in Chapter 2 and $\text{Cl}_4\text{P}(\text{N,N-diphenylbenzamidine})$ presented in Chapter 3. The use of the silylated pyridine ligands eliminates the problem of HCl generation and ammonium chloride salt formation, hence giving quantitative yields of 1-8.

The potential problem posed by HF generation in the preparation of compounds 2, 4, and 5 is alleviated by using the silylated form of these pyridinol ligands. When HF is generated, it reacts with PF_5 to form a very stable H^+PF_6^- species (eq.(8)) that is difficult to separate from the target compound.



The formation of H^+PF_6^- as a by-product has also been previously encountered in this study, including the preparation of $\text{F}_4\text{P}(\text{N,N-diphenylbenzamidine})$ in Chapter 5.

An attempt was made to prepare a chloro analogue of compound 5 to complete the series. Neither the protonated ligand nor the silylated ligand preparation afforded the intended product, $\text{Cl}_4\text{P}(2\text{-mercaptopyridine})$.

The final products (1-8) are all thermally stable solids (mp 80-170°C). These compounds are white (2-4, 6, 8) or a light yellow (1, 5, 7) in color and are extremely moisture sensitive. In both reactions (2) and (3) substitution at E accompanied by coordination of the pyridine nitrogen to the Lewis acid phosphorus center forms a

six-coordinate phosphorus. The ability of acidic PX_5 compounds to form adducts with Lewis bases is well established (e.g. PF_5 and pyridine (py) readily generate the neutral adduct $F_5P \cdot py$ containing a hexacoordinate phosphorus center). Like the carbodiimides (Chapter 3), these compounds readily hydrolyze, but they are resistant to nucleophilic substitution. For example, neither **1** nor **2** can be methylated at the phosphorus center using $(CH_3)_4Sn$. This lack of reactivity would indicate further evidence of hexacoordination of the phosphorus in **1** to **8**.

4.3.1 Structure of $Cl_4P(2\text{-methylaminopyridine})^2$

The structure of compound **1**, shown in Figure 4.2, has a hexacoordinate environment at phosphorus. Relevant metrical parameters for compound **1** are given in Tables 4.5 and 4.6.

Similar to other λ^6 -phosphoranes containing a small-bite chelating ligand, such as dimethylcarbamate or carbodiimide (Chapter 3), compound **1** deviates from ideal octahedral geometry around phosphorus. The small bite angle in **1** ($70.9(2)^\circ$) is almost the same as the bite angle of $Cl_2(CF_3)_2P(DCC)Cl$ ($70.7(2)^\circ$) described in Chapter 3. This small-bite angle allows more room for the chlorines to spread out around the phosphorus in the radial plane. For example, the $Cl(3)\text{-}P\text{-}Cl(4)$ angle is $97.39(9)^\circ$, which is larger than the 90° angles required for an ideal octahedral arrangement. The four chlorines around phosphorus bend slightly away from the methylamino group towards the pyridine ring with a $Cl(1)\text{-}P\text{-}Cl(2)$ angle of $177.2(1)^\circ$. Presumably this is a result of more steric demand generated by the methyl group on N(2) compared to the planar geometry of atoms around the pyridine nitrogen (N(1)).

The P-Cl bond distances are normal with a mean of $2.118 \text{ \AA}$. The P-N(2) bond distance ($1.763(4) \text{ \AA}$) is only slightly shorter than that expected for a P-N single-bond

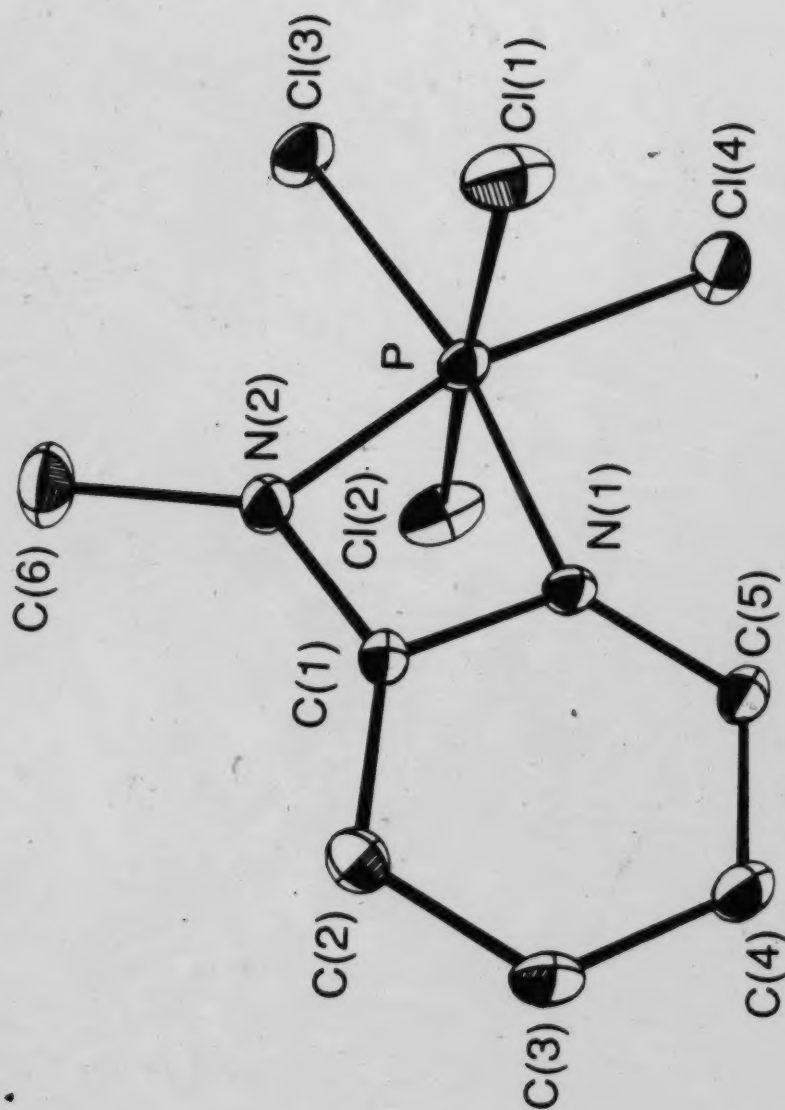
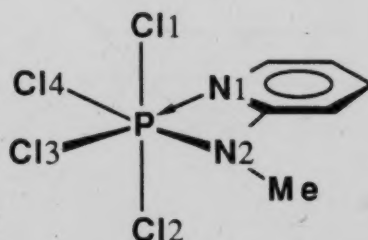


Figure 4.2 Perspective view of **1** showing atom labelling scheme. Atoms are represented by Gaussian ellipsoids at the 20% probability level. Structure courtesy of Dr. A. Pinkerton, Department of Chemistry, University of Toledo.

distance (1.78 Å) and the bond distance of 1.845(4) Å from phosphorus to the ring nitrogen (P-N(1)) is comparatively longer. This is expected because, the structure of **1** can be formally written with a single bond for P-N(2) and a dative bond for P-N(1).



The radial P-Cl bond distances differ apparently as a result of a *trans* influence from the two nitrogens. The shorter P-Cl(3) bond (2.077(2) Å) is *trans* to the heterocyclic ring nitrogen and the longer P-Cl(4) bond distance (2.103(2) Å) is *trans* to the N(2) nitrogen. The N(2) atom shows a planar arrangement of substituents (C(1), C(6), and P). This along with the short P-N(2) bond distance suggests that there is donation of electron density from the lone pair of electrons on the methylamino group to an empty d-orbital on the phosphorus center.

The bond distances within the pyridine ring and the N(2)-C(6) single-bond distance in the methylamino group are all normal. The C(1)-N(2) (1.344(6) Å) and C(1)-N(1) (1.350(6) Å) bond distances in the chelating ring fall well short of distances expected for C-N single-bond distance (1.47 Å) and are comparable to the partial C-N double bond distance (1.310 Å) found in $\text{Cl}_2(\text{CF}_3)_2\text{P}(\text{DCC})\text{Cl}$ of Chapter 3. This indicates delocalization of the N(1)-C(1)-N(2) system previously discussed in the structure of $\text{Cl}_2(\text{CF}_3)_2\text{P}(\text{DCC})\text{Cl}$.

The most intriguing feature of the structure of compound **1** is the planarity. All the atoms, with the exception of the axial chlorines (Cl(1) and Cl(2)) and the methyl hydrogens, are coplanar. The largest deviation from this is N(1), which sits 0.026(5) Å

below the least-squares plane formed by all these atoms. This planarity is a reflection of the extensive π -electron delocalization not only within the pyridine ring, but also extending to the chelating N(1)-C(1)-N(2)-P ring of compound **1**.

4.3.2 Nuclear Magnetic Resonance Spectra

The structures of the title compounds can be derived from their ^1H , ^{19}F , and ^{31}P NMR spectra and are illustrated in Figure 4.1. A summary of the NMR parameters of compounds **1** to **8** is given in Table 4.7. Although most of these pyridinol based phosphoranes are not fluxional at room temperature, some required low temperature conditions for NMR characterization. In all cases the low frequency ^{31}P NMR chemical shifts (-131.3 to -202.2 ppm) were characteristic of hexacoordinate phosphorus compounds.

All the tetrachloro compounds (**1**, **3**, and **7**) were immediately identified by ^{31}P NMR in solution by their low frequency shifts and characteristic couplings to the protons on the chelating ligand. For example, compound **1**, shown in Figure 4.3, resonates at -195.7 ppm, which is substantially lower than the chemical shift of its precursor, PCl_5 (-80 ppm).¹⁴ Similar low frequency chemical shifts for phosphorus have been observed for other tetrachloro- λ^6 -phosphoranes, such as the carbodiimide derivatives $\text{Cl}_4\text{P}(\text{DCC})\text{Cl}$ [-204.7 ppm] and $\text{Cl}_4\text{P}(\text{DPC})\text{Cl}$ [-205.2 ppm]. The ^{31}P NMR chemical shifts of these compounds (**1**, **3**, and **7**) shifts to lower field (higher frequency) as the electronegativity of the substituents ($\text{E} = \text{NPy}$, NCH_3 , O), increases in the series NPy [-202.2 ppm] < NCH_3 [-195.7 ppm] < O [-184.5 ppm]. The trend displayed here is an increased deshielding of the phosphorus center by the increased electron withdrawing ability of the chelating E substituent.

Table 4.7 NMR Parameters for compounds 1 to 8 and F₅P-Py.

Compound ^a	δ ¹ H ^b	ϕ ¹⁹ F ^c	σ ³¹ P ^d	³ J _{PH(A)} (Hz)	¹ J _{PF(ax)} (Hz)	¹ J _{PF(rad)} ¹ J' _{PF(rad)} (Hz)	other couplings (Hz)
1	8.20 ^e 3.31 ^f	—	-195.7	17	—	—	³ J _{PH(Mc)} = 27
2	7.60-7.74 ^e 2.29 ^f	-70.9 (2) ^{gh} -73.8 (1) ⁱ -89.0 (1) ⁱ	-132.4 ⁱ	j	827	838 862	² J _{F(ax)F(rad)} = 60 ² J _{F(ax)F'(rad)} = 65 ² J _{F(rad)F'(rad)} = 68
3	8.33 ^e	—	-184.5	16	—	—	—
4	8.03 ^e	k	-131.3 ^p	13.6	855 ^l	855 ^l	—
5	8.12 ^e	-117.8 (2) ^h -134.7 (1) ⁱ -159.3 (1) ⁱ	-136.4 ⁱ	14.5	968	747 1002	² J _{F(ax)F(rad)} = 47 ² J _{F(ax)F'(rad)} = 83 ² J _{F(rad)F'(rad)} = 55
6	7.75-7.85 ^e 3.22 ^f	-62.0 (1) ^m -67.2 (2) ⁿ	-152.2 ^o	j	—	—	² J _{PF(rad)} = 91 ² J _{PF(ax)} = 118 ² J _{FF} = 14
7	8.48 ^e	—	-202.2	15.5	—	—	—

Table 4.7 continued.

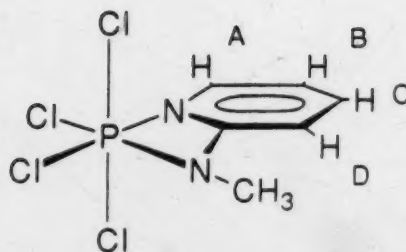
Compound ^a	δ $^1\text{H}^b$	ϕ $^{19}\text{F}^c$	σ $^{31}\text{P}^d$	$^3J_{\text{PH}}(\text{A})$ (Hz)	$^1J_{\text{PF}}(\text{ax})$ (Hz)	$^1J_{\text{PF}}(\text{rad})$ $^1J'_{\text{PF}}(\text{rad})$ (Hz)	other couplings (Hz)
8	8.12-8.20 ^{e,j} -75.4 (1) ⁱ -79.1 (1) ⁱ	-63.6 (2) ^h	-135.2 ⁱ	j	835	829 864	$^2J_{\text{F(ax)F(rad)}} = 58$ $^2J_{\text{F(ax)F'(rad)}} = 63$ $^2J_{\text{F(rad)F'(rad)}} = 67$
F ₅ P-Py			-144.2 ^r	6.8	788 ^s (cis)	759 ^s (trans)	—

^a in CDCl₃^b ppm relative to TMS^c ppm relative to CFC1₃^d ppm relative to 85% H₃PO₄^e ortho pyridine ring proton^f methyl group on amine^g at -50°C^h doublet of doublets of doubletsⁱ doublet of doublets of triples^j obscured by overlapping multiplets^k very broad signals^l fluorines fluxional^m doublet of septetsⁿ doublet of quartets^o septet of quartets^p pentet of broad lines^q hexet of broad lines^r at 22°C^s John, K-P; Schmutzler, R., *Z. Naturforsch.*, 1974, 29B, 730

In Figure 4.3 the phosphorus-proton couplings are displayed. The pattern is essentially an overlapping doublet ($^3J_{\text{PH(A)}} = 17 \text{ Hz}$) of quartets ($^3J_{\text{PH(Me)}} = 27 \text{ Hz}$), with coupling to the ortho ring proton and the amino methyl group, respectively. These $^3J_{\text{PH}}$ couplings are markedly different from each other and are larger than the usual $^3J_{\text{PH}}$ coupling constants.¹⁵ The $^3J_{\text{PH(A)}}$ coupling to the ortho ring protons in these compounds (1-8) ranges from 13.6 to 17 Hz, which is larger than the $^3J_{\text{PH(A)}}$ coupling constants found in similar compounds such as $\text{F}_5\text{P}\cdot\text{py}$ [6.8 Hz] and $\text{F}_4\text{P}(8\text{-hydroxyquinoline})$ [6.0 Hz]¹⁶. In both these cases, the lower $^3J_{\text{PH(A)}}$ coupling constant could arise as a result of electron density being drawn from the P-N bond by either the extra fluorine in $\text{F}_5\text{P}\cdot\text{py}$ or the larger conjugated ligand system in $\text{F}_4\text{P}(8\text{-hydroxyquinoline})$. The $^3J_{\text{PH(Me)}}$ coupling constant of 27 Hz is much larger than the general quoted range of 4-17 Hz for P-NCH_3 and is also larger than $^3J_{\text{PH(Me)}}$ found in $\text{Cl}_4\text{P}(\text{N}, \text{N}'\text{-dimethylcarbodiimide})\text{Cl}$ [20.8 Hz]. These $^3J_{\text{PH}}$ coupling constants in **1** suggest that the bonding of the two nitrogens to phosphorus is very different and that the lone pair of electrons on the methylamino nitrogen may be back-donating to empty 3d orbitals on phosphorus. The finer coupling observed as triplets (Figure 4.3) in this pattern is residual coupling to other ring protons of the chelate.

The ^1H NMR spectrum of the same compound (**1**) shown in Figure 4.4 confirms, by the presence of a methyl doublet, the coupling of the methylamino group to the phosphorus center. The smaller downfield signals due to the ring protons are expanded in Figure 4.5. The strong $^3J_{\text{PH}}$ couplings of both the ring proton ($\text{H}_{(\text{A})}$) and the methylamino proton ($\text{H}_{(\text{Me})}$) indicate that both nitrogens are bound to the central phosphorus. Each signal, in Figure 4.4, has been identified through selective decoupling experiments. As one compares the free 2-(trimethylsilyl-methylamino)pyridine ligand to the chelated ligand in **1** the introduction of phosphorus coupling is apparent. The J_{PH} couplings found in this spectrum correspond to the J_{PH} couplings listed in Figure 4.3. Note that the J_{PH} couplings are observed for ring protons $\text{H}_{(\text{A})}$, $\text{H}_{(\text{B})}$, and $\text{H}_{(\text{C})}$, but not for $\text{H}_{(\text{D})}$ even though $\text{H}_{(\text{D})}$ is

^{31}P NMR (161.98 MHz)



22° C

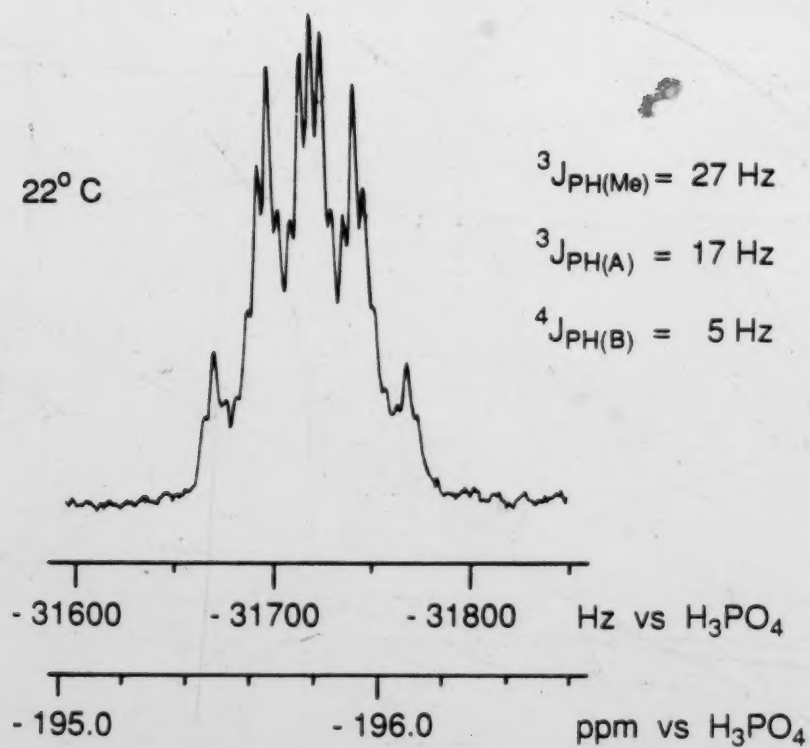


Figure 4.3 The ^{31}P NMR spectrum of **1** showing coupling to the ligand protons.

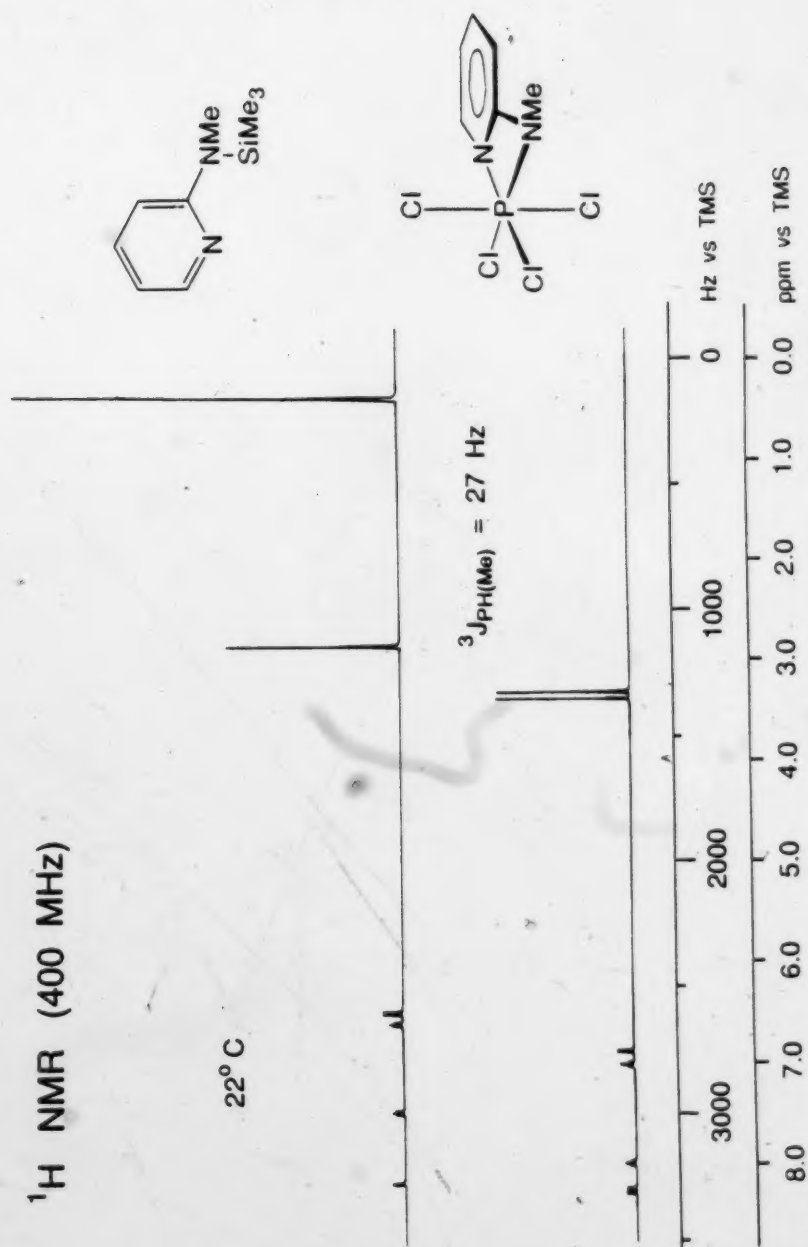


Figure 4.4 A comparison of the ¹H NMR spectra of 2-(N-trimethylsilyl-N-methylamino)pyridine ligand and compound 1.

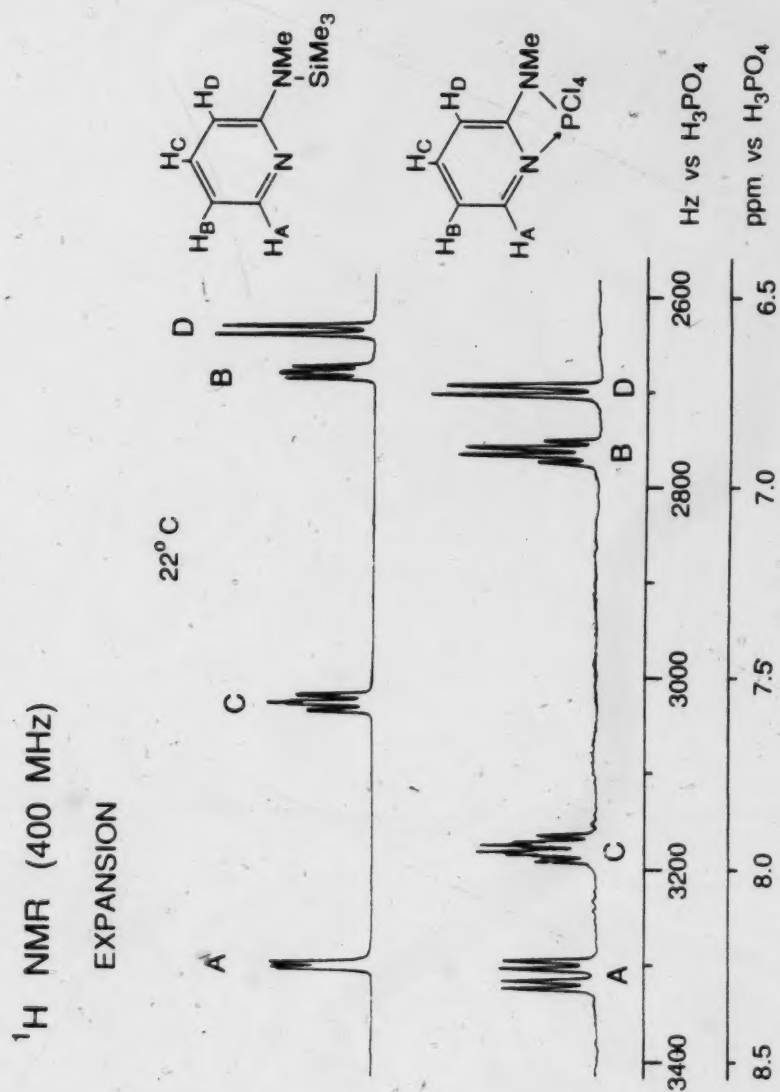


Figure 4.5 Expansion of the ring-proton region in the ¹H NMR spectra of 2-(N-trimethylsilyl)-N-methylamino)pyridine ligand and compound **1**.

closer to phosphorus by one bond length than is $H(C)$. This is an indication of electron density being drawn away from that part of the pyridine ring attached to the methylamino group. Similar data were also collected from **3** and **7** and are listed in Table 4.7.

The phosphorus signal of **6** [-152.2 ppm] is split into a septet of quartets by fluorine coupling to two different CF_3 groups. Two signals appear in a 2:1 ratio (-67.2 and -62.0 ppm) in the ^{19}F NMR spectrum in the expected doublet of quartets and doublet of septets coupling patterns. The two equivalent CF_3 groups have a larger $^2J_{PH}$ coupling constant (118 Hz) than does the third CF_3 group (91 Hz). This indicates that two of the CF_3 groups are axial and one is radial (see Section 3.3.3). This is also the preferred orientation that has been observed in several other compounds where hexacoordinate phosphorus centers contain three CF_3 groups and a small-bite chelating ligand; examples include $F(CF_3)_3P(O_2CN(CH_3)_2)$,¹⁷ $CH_3(CF_3)_3P(O_2CN(CH_3)_2)$,¹⁸ and $Cl(CF_3)_3P(DCC)Cl$.¹⁹ Although the multinuclear NMR data structurally characterize **6**, they cannot unambiguously identify the relative positions of the radial ligands CF_3 and Cl with respect to the methylamino group. For this characterization an X-ray crystallographic structure is required.

The tetrafluoro analogues (**2**, **4**, **5**, and **8**) can also be identified by their low frequency ^{31}P NMR chemical shifts (-131.3 to -136.4 ppm). Analogous phosphorus chemical shifts have been reported for other tetrafluoro- λ^6 -phosphoranes, such as $F_4P(acac)$ [-148.7]²⁰, $F_4P(dimethylbenzamidine)$ [-137.0]²¹, and $F_4P(8-hydroxyquinolone)$ [-118.7 ppm].²² Similar to the tetrachloro compounds, the tetrafluoro analogues (**2**, **4**, **5**, and **8**) display the same trend in their ^{31}P NMR chemical shifts with respect to the electronegativities of their E groups ($E = S, NPy, NCH_3, O$). The resonance frequency increases in the series, S [-136.4 ppm] < NPy [-135.2 ppm] < NCH_3 [-132.4 ppm] < O [-131.3 ppm], in the same order as the tetrachloro derivatives. These chemical shift trends reflect the relative amounts of phosphorus deshielding introduced by various E

groups. Other trends, such as fluxionality of these compounds (**2**, **4**, **5**, and **8**) discussed later in Section 4.3.3 have also been linked to relative electron withdrawing abilities of the E groups.

Compounds **2** and **4** displayed fluxional behavior with rapid exchange of the fluorine at room temperature. This sort of fluxional behavior has been observed in the λ^6 -(carbamato)phosphoranes, which also have a four-membered chelating ring.²³ In the carbamate system, it is proposed that this strained four-membered ring opens to form a pentacoordinate phosphorus center and allow the exchange of the ligands.²³

The ^{31}P NMR signals in compounds **2** and **4** appear as pentets of broad lines at ambient temperatures. Although the exchange in **4** could not be 'frozen out', it was possible to do so for **2**. Figure 4.6 shows the ^{31}P NMR spectrum at ambient temperature as a pentet of broad lines, and at -50°C as a resolved doublet of doublets of triplets. This splitting pattern indicates three different fluorine environments around phosphorus in a 1:1:2 ratio. That is, there are two different radial fluorines, one trans to a ring nitrogen and one trans to the methylamino group, and two equivalent axial fluorines. This is also confirmed by the ^{19}F NMR spectrum of **2**, which shows three separate fluorine signals (Table 4.7).

Compounds **5** and **8** do not display fluxional behavior at room temperature, making their characterization straightforward. For example, **5** resonates at -136.4 ppm (Figure 4.7) and displays a doublet of doublets of triplets splitting pattern similar to **2**. Again, this is due to three different fluorine environments in a 2:1:1 ratio. The ^{19}F NMR spectrum of **5** confirms this (Figure 4.8 and 4.9). Three separate fluorine signals are observed. The signal due to the two axial fluorines (-117.8) shows coupling to phosphorus and to two different radial fluorines. The signals due to each of the radial fluorines (-134.7 and -159.3 ppm) are coupled to phosphorus, the two axial fluorines, and to each other (Figure 4.9), resulting in a doublet of triplets of doublets. (The signal at -159.3 ppm is overlapping and appears as a doublet of quartets). Although the NMR spectrum cannot definitively allow assignment of

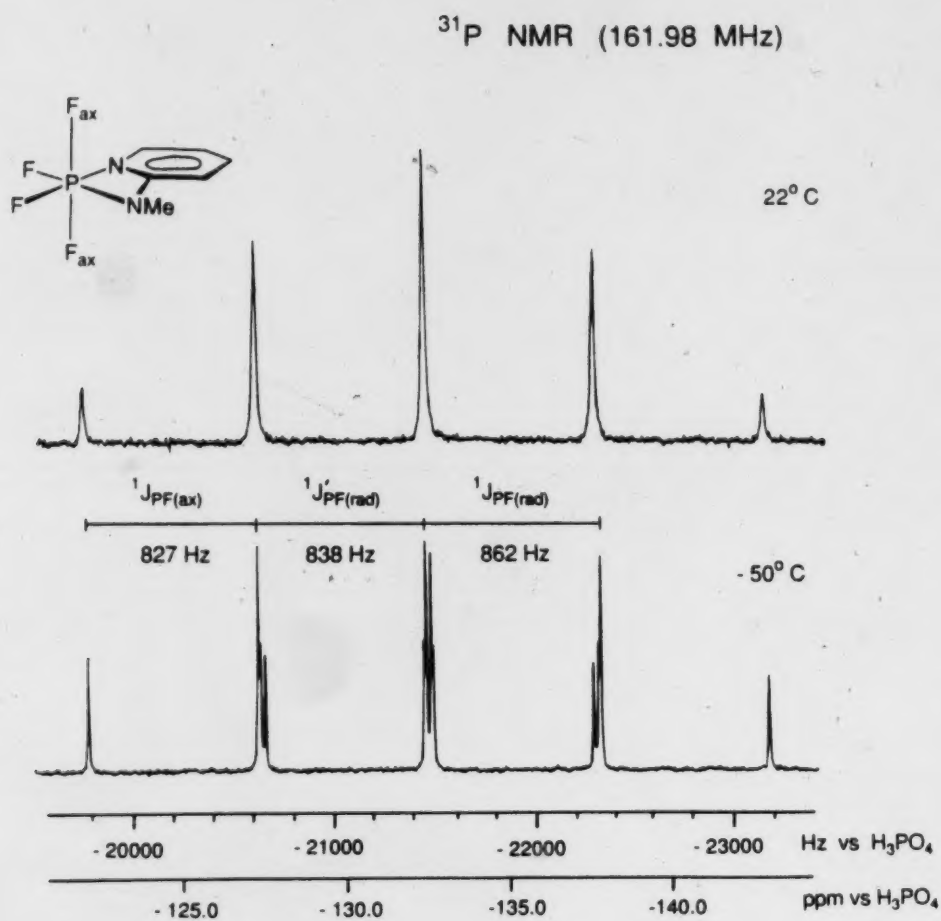


Figure 4.6 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4** at ambient temperature (22° C) and at -50° C.

^{31}P NMR (161.98 MHz)

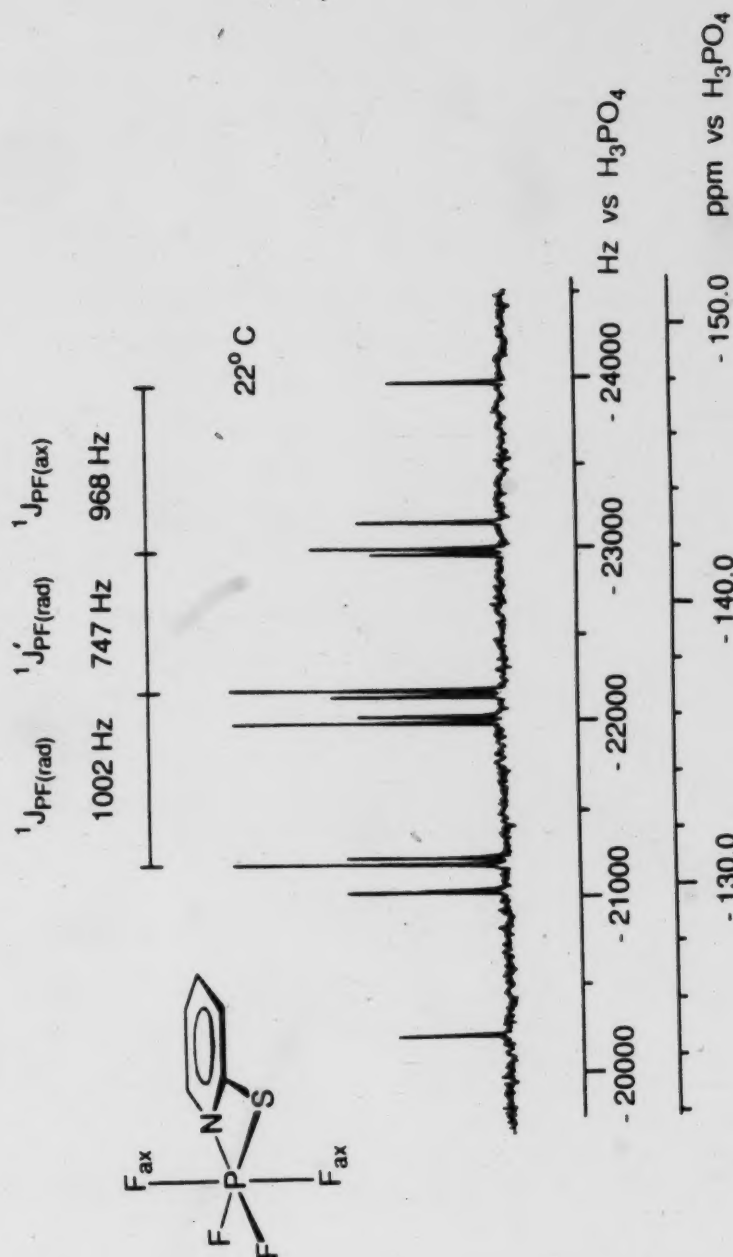


Figure 4.7 The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of compound 5.

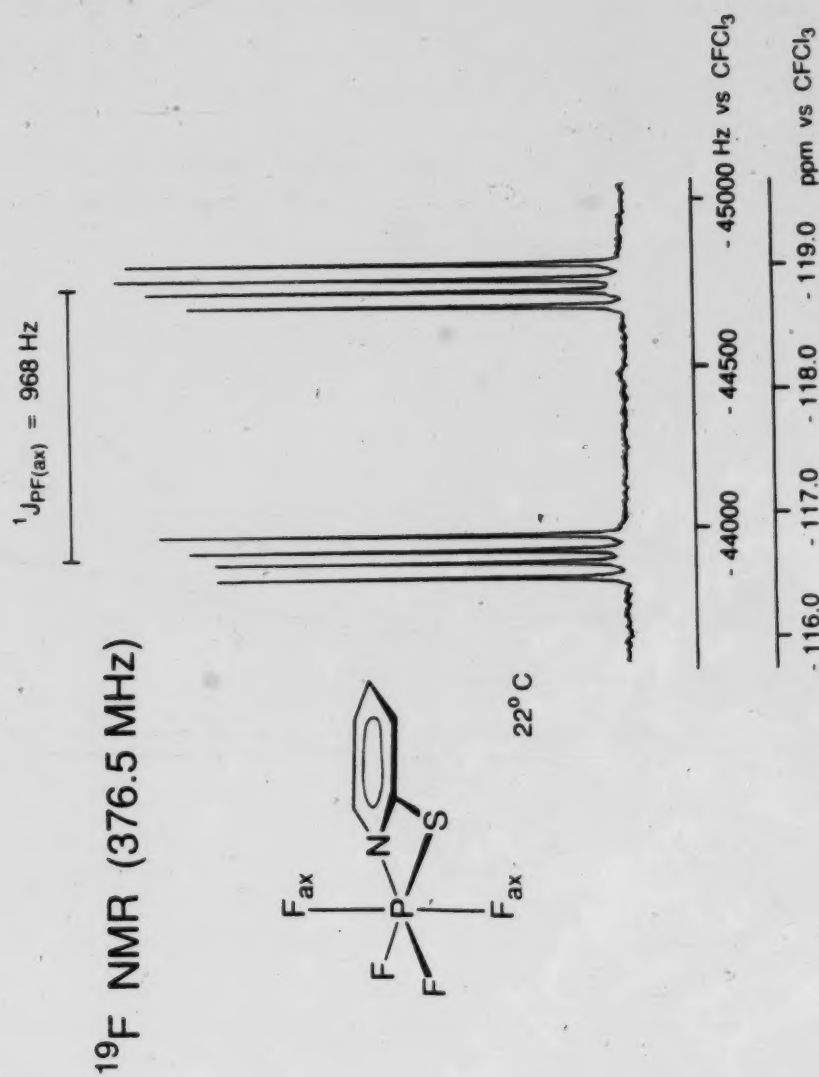


Figure 4.8 The ^{19}F NMR spectrum of 5 showing the signal corresponding to the axial fluorines (F_{ax}).

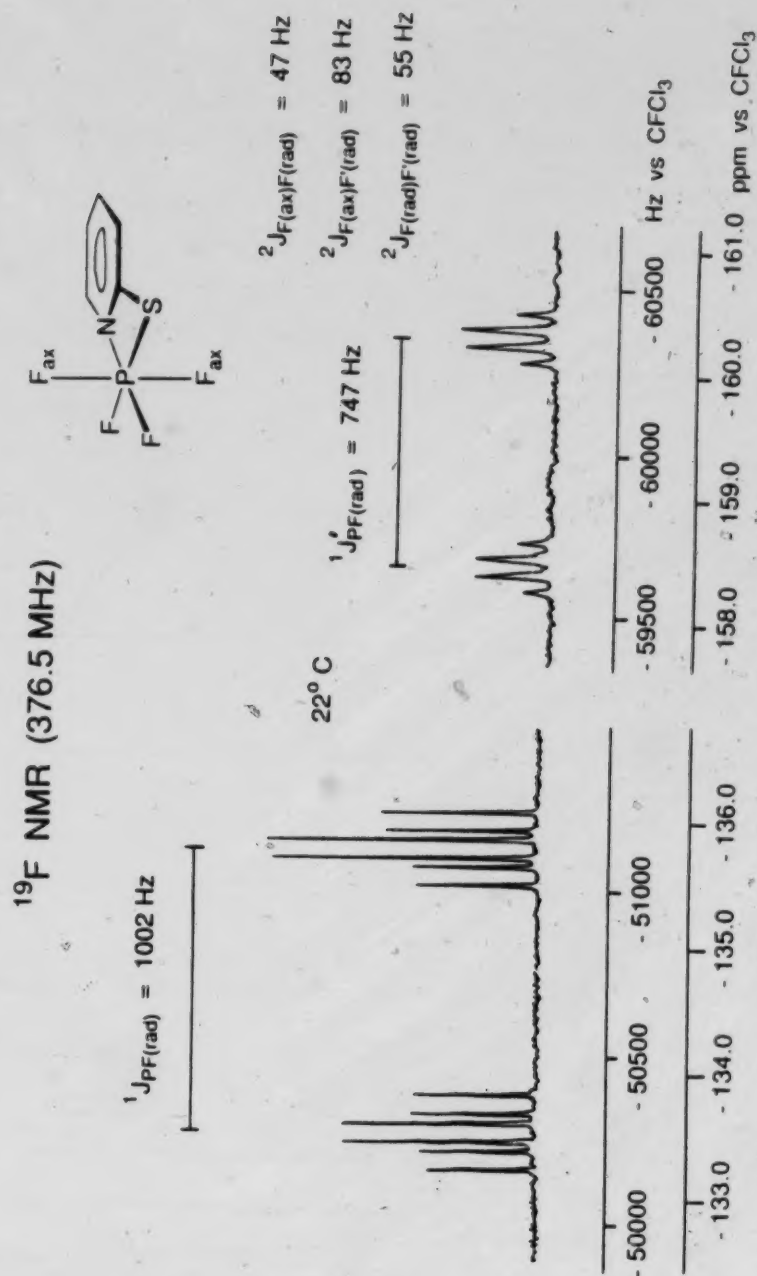


Figure 4.9 The ^{19}F NMR spectrum of **5** showing the two signals corresponding to the radial fluorines.

the specific signal of each radial fluorine, it does confirm the structure of these compounds as those shown in Figure 4.1. Similar patterns are also observed for compound 8 (Table 4.7).

4.3.3 Fluxional Behavior

The NMR spectra (Section 4.3.2) of the fluoro analogues (2 and 4) show exchange of their fluorine environments at room temperature. Using a spin saturation transfer (SST) experiment at 243K (-30°C) the barrier to fluorine exchange for compound 2 was calculated to be 56.4(5) kJ/mol. This technique may be employed when the spin-lattice relaxation (T_1) of a nucleus is comparable to the rate of exchange. In the case of compound 2, one fluorine signal is saturated and with partial exchange an intensity decrease in the other fluorine signals can be observed. If exchange is too rapid, as in the case of 4, the other sites become completely saturated. If exchange is too slow, as in the case of 5, no measurable decrease in signal intensity can be observed.

Figure 4.10 shows the three ^{19}F NMR spectra collected in the spin saturation transfer experiment. Spectrum (a) of Figure 4.10 displays the ^{19}F NMR signals corresponding to two equivalent axial fluorines and two different radial fluorines. Spectrum (b) of Figure 4.10 shows saturation at -69.6 ppm (axial fluorine) and partial saturation transfer to the radial fluorines at -72.4 ppm and -88.1 ppm. Finally, spectrum (c) of Figure 4.10 is a difference spectrum, (a) minus (b). From the integrated intensities of (b) and (c) the magnitudes of the magnetizations can be determined for the rate constant (k) calculation. In addition, the spin-lattice relaxation time (T_1) of the fluorines is also required for the rate constant determination. This rate constant (k) was used to eventually calculate the free energy of activation ($\Delta G^\ddagger$) of this fluorine exchange process. Detailed calculations can be found in Section 4.2.12 of the Experimental. The barrier to exchange in 2 is slightly larger than the $\Delta G^\ddagger$ reported for $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ [56(2)]

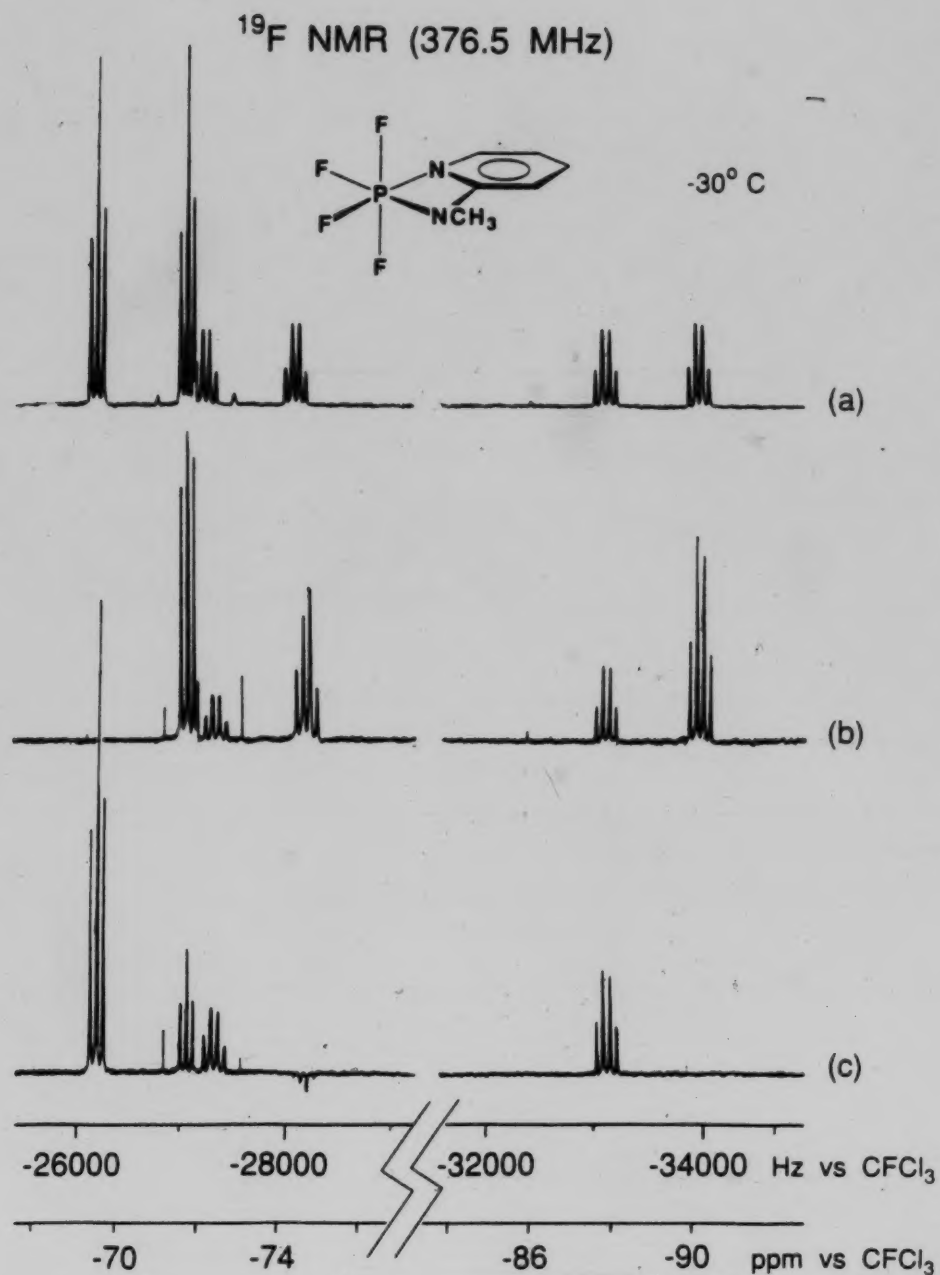


Figure 4.10

The ^{19}F NMR spectra of **2** (at -30° C) in the spin saturation transfer experiment showing: (a) normal spectrum; (b) ^{19}F (saturated at -69.6 ppm) spectrum; and (c) difference spectrum [(a) - (b)].

$\text{kJ/mol}]$.²³ Although the substituents are very different, both **2** and $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ are neutral compounds with a hexacoordinate phosphorus center formed by a small-bite chelating ligand, which can undergo a ring opening followed by a pseudorotation.

A selective inversion transfer (SIT) experiment, which is another magnetization transfer experiment, was also employed to determine more reliably the $\Delta G^\ddagger$ of fluorine exchange in **2**. This SIT experiment will show the change in the magnitude of M_z values for all three fluorine sites as a function of time. Conversely, the SST experiment only shows transfer of saturating z-magnetization at one point in time. Although more measurements are required for the SIT experiment, it also yields more information about the mechanism of the exchange. The magnetization of one of the radial fluorines (F'_{rad}) at -89.0 ppm was inverted and the z-magnetizations (M_z) of the other two sites (F_{ax} and F_{rad}) were observed. Table 4.8 lists the z-magnetizations observed at each fluorine site as a function of time. Using a modelling program developed by Muhandiram and McClung the actual M_z values were compared to simulated M_z values generated by various exchange mechanisms.¹⁰

If it is presumed that the scrambling of fluorines in **2** arises from a dissociation of the chelate at the base (pyridine nitrogen) forming a λ^5 -phosphorus center and this λ^5 -phosphorus compound then undergoes a pseudorotation (Figure 4.11) in which the axial and radial fluorines exchange, a model with a rate constant k_1 is created.

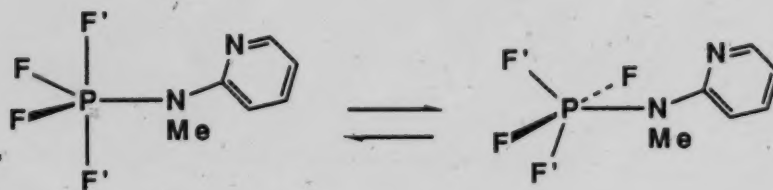


Figure 4.11 Pseudorotation of **2** Exchanging Axial and Radial Fluorines

Table 4.8 M_z values and time for three fluorine sites in 2.

Time (s)	$M_z^a(F_{ax})$	$M_z^a(F_{rad})$	$M_z^a(F'_{rad})$
0.001	406.22	193.03	-152.78
0.002	400.75	194.06	-128.67
0.004	395.87	194.06	-143.34
0.010	397.80	183.79	-125.68
0.020	383.05	175.73	-90.35
0.040	377.32	160.44	-64.39
0.100	350.14	129.27	22.49
0.200	330.74	119.36	77.27
0.400	312.05	125.83	119.42
0.600	315.60	147.27	147.37
1.000	344.13	172.25	168.31
2.000	382.94	200.63	190.22
5.000	409.16	217.19	207.40

^a Z-magnetization in arbitrary units.

Figure 4.12 shows the actual z-magnetizations measured (Δ O Δ) and the calculated z-magnetizations (solid line) based on the model: ring opening with pseudorotation. The extremely poor fit, of actual and calculated data, indicates that the fluorine exchange cannot be accounted for by this model.

Another possible exchange mechanism is a 180° rotation of the bidentate chelating ligand after ring opening to the λ^5 -phosphorane (Figure 4.13). This mechanism (rate constant = k_2) would effectively exchange radial fluorines.

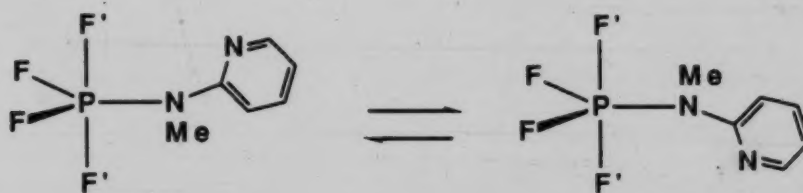


Figure 4.13 180° Rotation of the Bidentate Chelating Ligand Exchanging Radial Fluorines.

The poor fit using just radial exchange, shown in Figure 4.14, suggests that this model cannot account for the observed M_z values.

Finally a combination of ligand rotation (Figure 4.13) and phosphorus pseudorotation (Figure 4.11) was used as a model. Figure 4.15 shows a good fit of actual and calculated M_z values with this combination of mechanisms for fluorine exchange. Transfer of z-magnetization to the radial fluorine compared to the axial fluorine is quicker. This is reflected in the earlier dip found in the 'Rad' line compared to the 'Ax' line shown in Figure 4.15. The rate constants were determined to be $k_1 = 1.9(1)$ and $k_2 = 4.4(3)$ for pseudorotation and ligand rotation, respectively. The corresponding $\Delta G^\ddagger$ values were calculated to be $\Delta G_1^\ddagger = 57.8(1)$ and $\Delta G_2^\ddagger = 56.1(1)$ kJ/mol using equation (2) (see Section 4.2.12 of Experimental). Again these values are both similar to $\Delta G^\ddagger$ for $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ [56(2) kJ/mol].²³

^{19}F (376.5 MHz) NMR

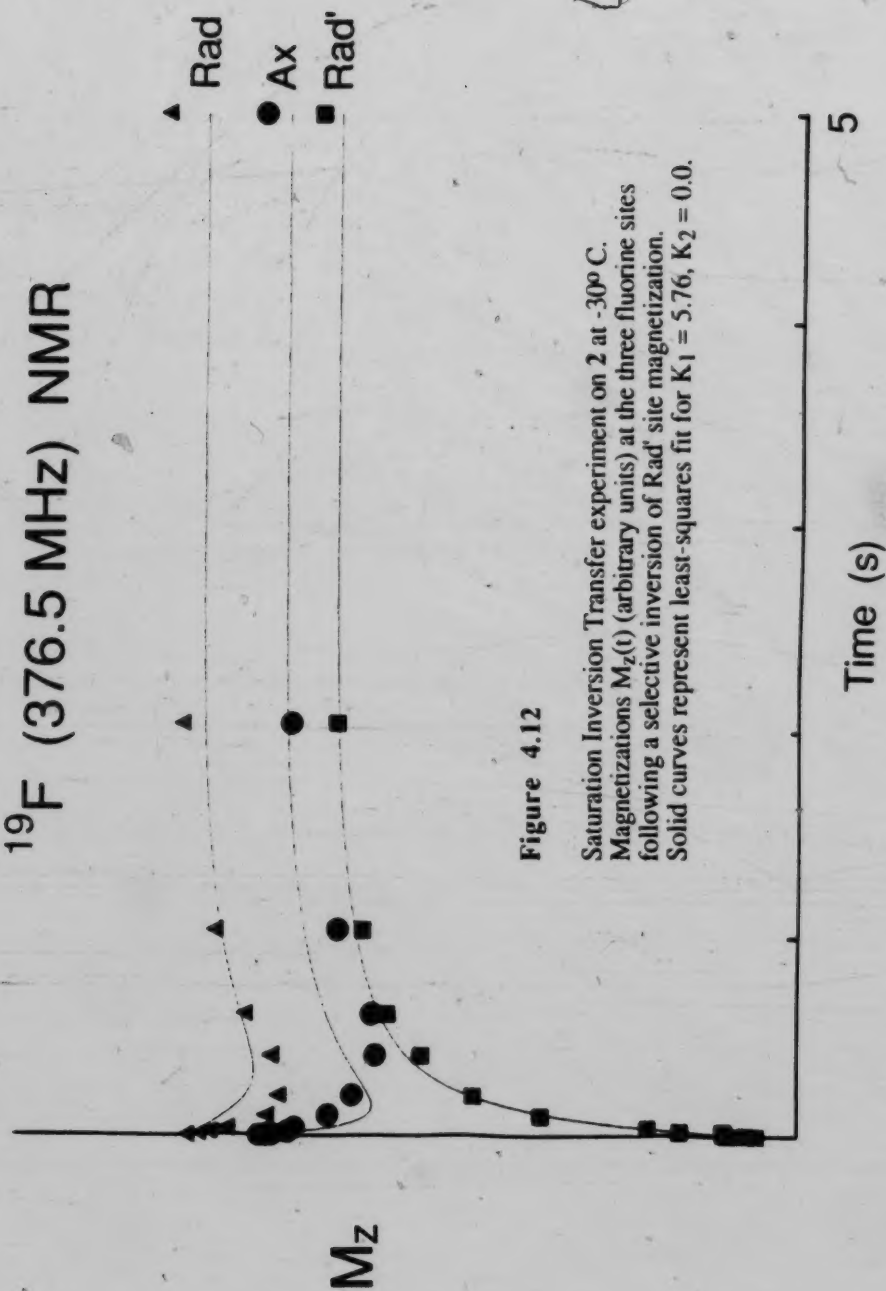


Figure 4.12

Saturation Inversion Transfer experiment on 2 at -30°C .
Magnetizations $M_z(t)$ (arbitrary units) at the three fluorine sites
following a selective inversion of Rad' site magnetization.
Solid curves represent least-squares fit for $K_1 = 5.76$, $K_2 = 0.0$.

^{19}F (376.5 MHz) NMR

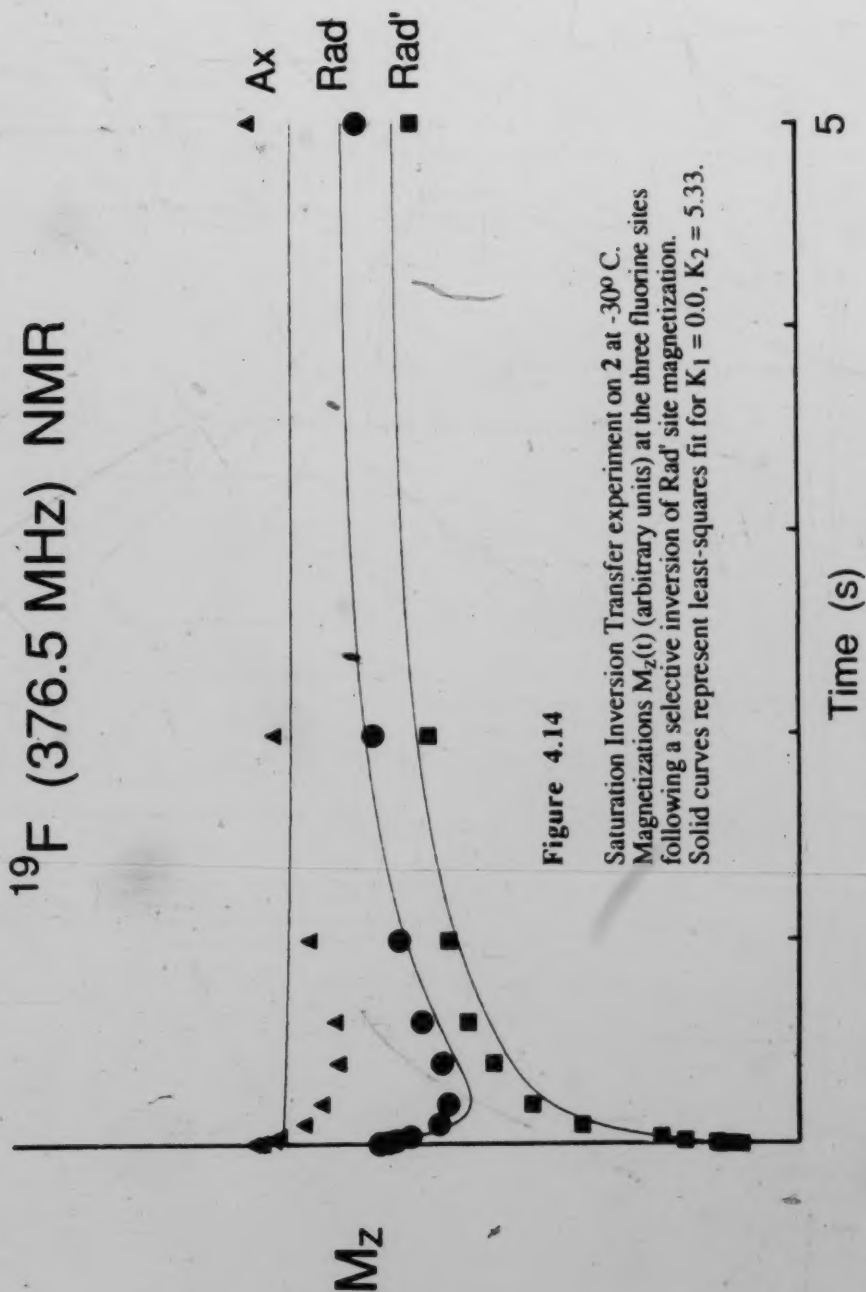


Figure 4.14

Saturation Inversion Transfer experiment on 2 at -30°C . Magnetizations $M_z(t)$ (arbitrary units) at the three fluorine sites following a selective inversion of Rad' site magnetization. Solid curves represent least-squares fit for $K_1 = 0.0$, $K_2 = 5.33$.

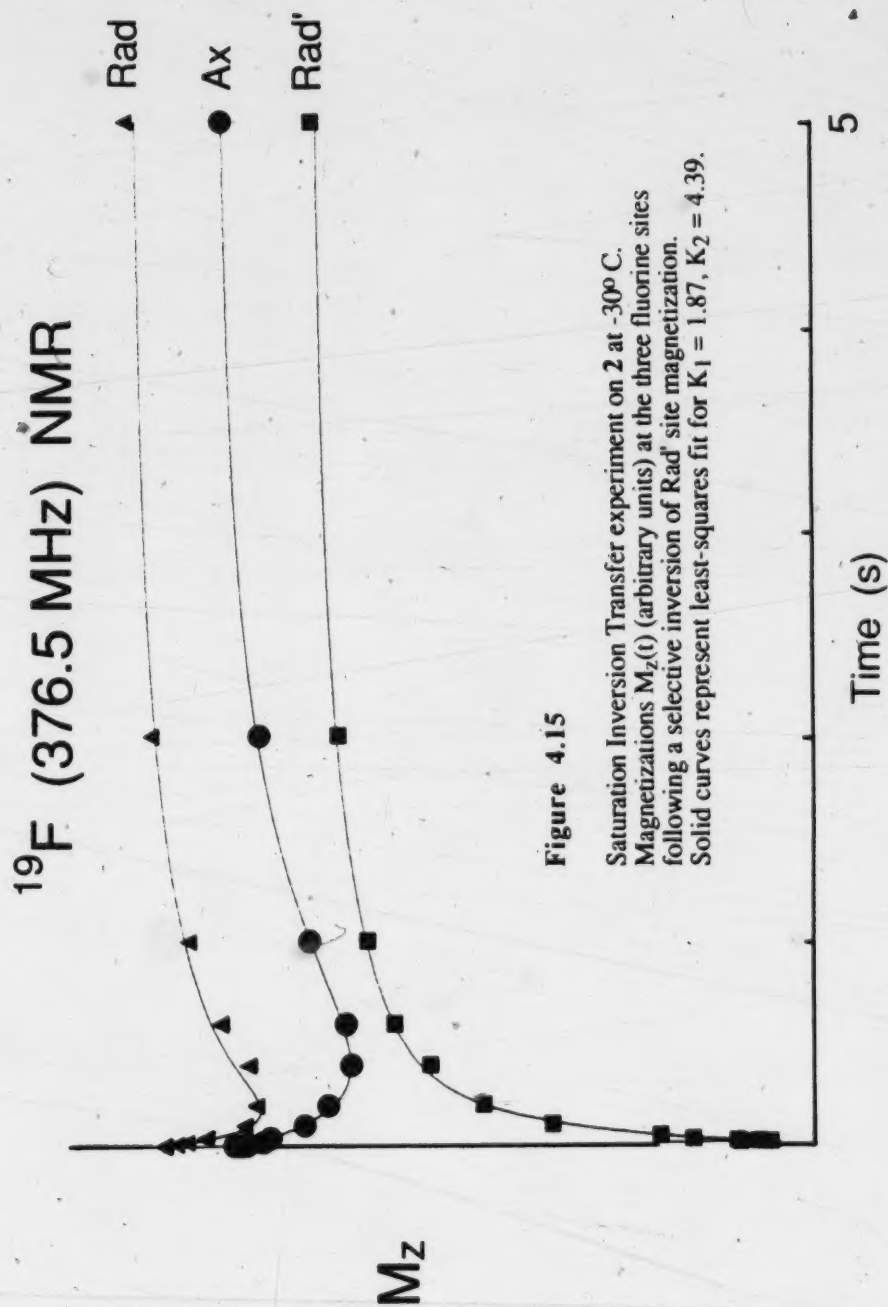
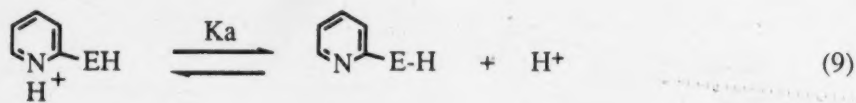


Figure 4.15

Saturation Inversion Transfer experiment on **2** at -30°C . Magnetizations $M_z(t)$ (arbitrary units) at the three fluorine sites following a selective inversion of Rad' site magnetization. Solid curves represent least-squares fit for $K_1 = 1.87$, $K_2 = 4.39$.

The selective inversion transfer experiment not only determines the energy barrier to the fluorine exchange, it also strongly suggests that there are two mechanisms operating simultaneously. The CF_3 group exchange in $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$ showed only a pseudorotation mechanism with no evidence of a radial position exchange mechanism. However, even if such a radial exchange mechanism did exist in $\text{CH}_3(\text{CF}_3)_3\text{P}(\text{O}_2\text{CN}(\text{CH}_3)_2)$, it would be undetectable by this method, because N, N-dimethylcarbamate is a symmetric ligand which makes the radial sites chemically equivalent.

The ease of this ring opening and consequently the rate of fluorine scrambling increases with the electronegativity of the E substituent (where $\text{E} = \text{O}, \text{NCH}_3, \text{NPy}, \text{S}$). That is, both the relative exchange rate and the electronegativity follow the trend $\text{O} > \text{NCH}_3 > \text{NPy} > \text{S}$. By drawing electron density away from the pyridine nitrogen to itself, the E substituent affects the ability of the pyridine to coordinate to the Lewis acid phosphorus center, thus increasing the rate of fluorine exchange. The trend in E group electronegativities is also evidenced by the increased deshielding of the phosphorus chemical shift discussed previously in Section 4.3.2. It is noteworthy to mention that the pK_a values of the corresponding free ligand pyridinium ions (eq.(9)) decrease in the same order.



These values are a reflection of the basicity of the ring nitrogen. The larger pK_a value indicates a more basic ring nitrogen center, which in turn results in slower fluorine exchange. This trend is summarized in Table 4.9.

Table 4.9 The pKa's of  E-H, phosphorus chemical shifts and fluxionality of corresponding F₄P compounds.

E	$\sigma^{31}\text{P}$ (ppm)	pKa ^a	Rate of Exchange
O	-131.3	0.75 ²⁴	Fast Slow
N(CH ₃)	-132.4	~ 6.7 ²⁵ (NH) ^b	
N(Py)	-135.2	7.14 ²⁶	
S	-136.4	9.69 ²⁷	

^a Proton loss from the pyridine nitrogen at 20° C.

^b Value for 2-(methylamino)pyridine was unavailable.
The value for 2-aminopyridine is reported.

4.3.4 Ligand Modification

Unlike ligands in other series of neutral hexacoordinate phosphorus compounds, this series of pyridine-based ligands offers more versatility with respect to chemical modifications. In previous studies the collection of substituents around the central phosphorus was altered for a given bidentate chelate. For example, the λ^6 -(acetylacetonato)phosphoranes (Chapter 2) of the general formula F_{4-n}(CF₃)_nP(acac) (n = 0-3) and CH₃(CF₃)₃P(acac) give a complete series of mixed F and CF₃ substituents around phosphorus for a given bidentate ligand. Alterations of the chelating ligand were explored briefly for CH₃(CF₃)₃P(acac), CH₃(CF₃)₃P(aminoacac), and CH₃(CF₃)₃P(N-methylaminoacac); however, the complete series could not be generated.

In this chapter the pyridine-based ligands generated a comprehensive series of λ^6 -phosphoranes by exchanging the E group atom or the substituents on E of the ligand. The first point has been demonstrated, namely, S, O, and N have been used as chelating atoms (Figure 4.1). A trend in both the ^{31}P NMR chemical shifts and the fluxionality of these derivative was both observed and discussed (Section 4.3.3). In addition, modification of the E groups without using a different chelating atom was demonstrated by using the 2-(methylamino)pyridine and dipyridylamine ligands. Changing the substituent on the amino group altered the nature of the compound, as was shown in the difference in fluxional behavior in compounds 2 and 8.

4.4 Conclusion

This chapter presented the synthesis and characterization of a series of neutral hexacoordinate phosphorus compounds (1-8) containing a strained four-membered ring. These compounds were principally characterized by multinuclear NMR and all possessed a characteristic low-frequency chemical shift in their ^{31}P spectra.

Some of these compounds (2 and 4) displayed fluxional behavior at room temperature and were compared to the (dimethylcarbamato)phosphoranes and the (carbodiimide)phosphoranes (Chapter 3), which are both also four-membered ring systems. Using a spin saturation transfer experiment (SST), the energy barrier to the fluorine exchange was determined to be 56.9(5) kJ/mol for compound 2. However, using a selective inversion transfer (SIT) experiment it was discovered that two mechanisms of fluorine exchange are operating in compound 2. The energy barriers for these two mechanisms of fluorine exchange were calculated to be 57.8(1) and 56.1(1) kJ/mol at -30°C for pseudorotation fluorine exchange and radial fluorine exchange, respectively. It was discovered that as the electron-withdrawing capability of the substituent of the number

2 pyridine ring position increased, the rate of exchange of the fluorines and the phosphorus chemical shift increased.

The X-ray crystal structure of $\text{Cl}_4\text{P}(\text{2-methylaminopyridine})$ (**1**) shows a hexacoordinate geometry around the phosphorus center in the solid state. With the exception of the methyl hydrogens and the axial chlorines, all the atoms in **1** are coplanar indicating strong π -electron delocalization in the pyridine ring and the chelating ring on phosphorus.

Finally, it was shown how this ligand system could be systematically modified in several ways to prepare an entire spectrum of related chelates with subtle chemical differences. Indeed, exploitation of this ligand system provides a systematic method of exploring trends in the nature and formation of neutral λ^6 -phosphorus compounds.

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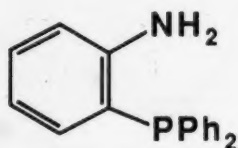
CHAPTER V

FUTURE PROSPECTS

The formation of an extensive series of neutral compounds containing a hexacoordinate phosphorus center, with the chelating ligands acetylacetone, carbodiimide, and pyridinol, has been discussed and summarized in Chapters 2, 3, and 4, respectively. This research represents a comprehensive segment of ongoing investigations into the nature of high oxidation / high coordinate phosphorus compounds. Although this work has shed light on many aspects of λ^6 -phosphorane chemistry, it has also led to more questions. There are several avenues open to future work, but this chapter will briefly outline three major areas of λ^6 -phosphorane studies that should be pursued.

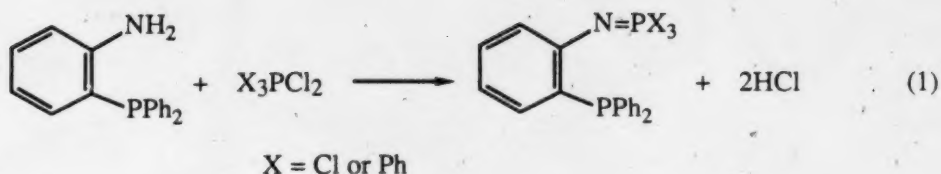
5.1 Search for Novel Chelating Ligands

As part of the continuing study of λ^6 -phosphoranes, it would be desirable to be able to generate new heterocycles containing a hexacoordinate phosphorus center. In the past oxygen, nitrogen, and sulfur have served as chelating atoms in this class of phosphorus compounds. Other elements, such as phosphorus or arsenic, should be considered as alternative chelating atoms.

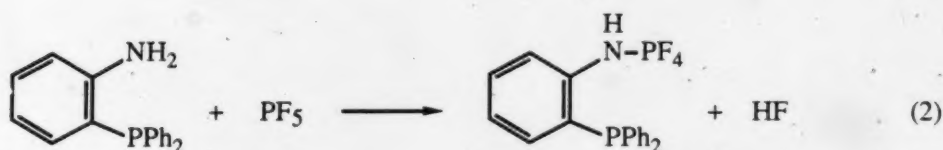


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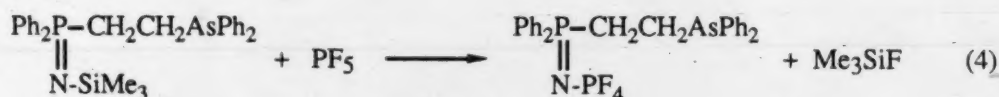
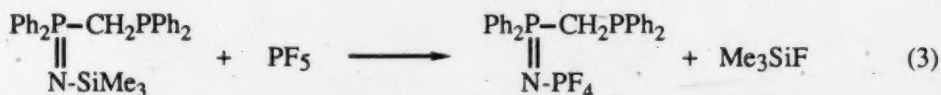
A chelate ligand such as (2-aminophenyl)diphenylphosphine (**1**) has been previously used to form platinum complexes.¹ Attempts to generate a λ^6 -phosphorane containing a P(III)-P(V) bond using this bidentate ligand (**1**) have been carried out in this work, however, the initial studies showed that **1** produced a tetracoordinate center via a Kirsanov reaction when combined with PCl_5 or Ph_3PCl_2 (eq.(1)).



A pentacoordinate phosphorus center is formed in the reaction of PF_5 with **1** (eq.(2)). The basic phosphorus center of the diphenylphosphino group did not coordinate to the Lewis acid $-\text{PF}_4$ center and so a λ^6 -phosphorane was not formed.



This result suggests that even if the amino group was protected (e.g. by methylation to $-\text{N}(\text{Me})\text{H}$) to prevent a Kirsanov reaction, the diphenylphosphino group would likely not coordinate to the phosphorus(V) center to form a λ^6 -phosphorane. This has also been observed in the reaction of PF_5 with the new heterodifunctional ligands $\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2\text{PPh}_2$ and $\text{Me}_3\text{SiN}=\text{PPh}_2(\text{CH}_2)_2\text{AsPh}_2$.^{2,3} Substitution occurs at the nitrogen with facile elimination of Me_3SiF (eqs.(3) and (4)); however, no evidence of the diphenylphosphino or diphenylarsino group coordination to the $-\text{PF}_4$ center could be found.



The basicity of the $-\text{AsPh}_2$ or $-\text{PPh}_2$ group is insufficient for coordination to the $-\text{PF}_4$ center. Adducts of PF_5 and phosphines have been reported for $\text{PH}_n\text{Me}_{3-n}$ ($n = 0-3$),⁴ but the corresponding phenylphosphine and phenylarsine adducts are unknown.

Since the $\text{F}_5\text{P}\cdot\text{PMe}_3$ adduct is known, it would be of interest to pursue the preparation of ligands containing the more basic and less sterically hindered dimethylphosphino group, such as $\text{Me}_3\text{SiN}=\text{PPh}_2\text{CH}_2\text{PMe}_2$ or $\text{Me}_3\text{SiN}=\text{PMe}_2\text{CH}_2\text{PMe}_2$ and the Me_2P analog of **1**. These types of ligands would readily substitute at the nitrogen and would possess a strong tendency for phosphine ($-\text{PMe}_2$) coordination to $-\text{PF}_4$ to form a hexacoordinate phosphorus center containing a P(III)-P(V) bond. It would therefore be worthwhile to investigate and expand the chemistry of these ligands with highly oxidized phosphorus with a view to expanding the range of λ^6 -phosphoranes.

5.2 Chemical Reactivity of λ^6 -Phosphoranes

Although several neutral compounds containing a hexacoordinate phosphorus center have been prepared and well characterized, very little research has been devoted to their chemical reactivity. Initial studies (Chapter 3) reveal that λ^6 -phosphoranes seem to resist simple nucleophilic substitutions. Alkyl lithium reagents have been used successfully in substitutions of the ring chlorine in $\text{Cl}_4\text{P(DPC)Cl}$, and the phosphorus chlorines can be exchanged for fluorines using AgF . Could substitution at the phosphorus be generated by other reagents, such as $(\text{CF}_3)_2\text{Hg}$, $\text{CF}_3\text{CH}_2\text{ONa}$, or $\text{LiN}(\text{SiMe}_3)_2$? In addition, the incorporation of a metal into these λ^6 -phosphorane compounds has not been investigated. Trial reactions of reagents such as $\text{Me}_3\text{SiOREO}_3$, and NaMn(CO)_5 may lead to novel classes of hexacoordinate phosphorus compounds involving a metal.

Finally, since the P-Cl bond of λ^6 -phosphoranes lacks reactivity (especially toward abstraction of Cl^-), one could perhaps attempt to incorporate an additional heteroatom into

the chelating ring. For example, the carbodiimide ring in $\text{Cl}_4\text{P}(\text{DPC})\text{Cl}$ may allow the introduction of a boron atom between the phosphorus and nitrogen when combined with BCl_3 .

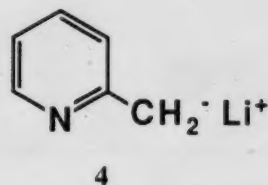
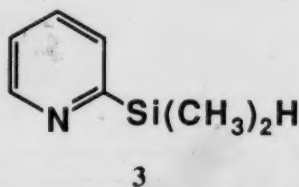
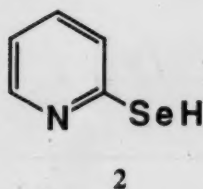
5.3 The Pyridinol Ligands

As alluded to in Chapter 4, the pyridine-based ligands are more versatile than the previously used chelates for the preparation of λ^6 -phosphorus centers.

The pyridine-based ligands can be modified by:

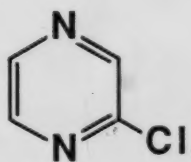
- (1) attaching different groups to the pyridine ring;
- (2) changing the atoms within the ring itself to form other six-membered heterocycles such as pyrazine or pyrimidine;
- (3) modifying the E group in the 2 position with other substituents (e.g. $\text{N}(\text{CH}_3)$, $\text{N}(\text{CH}_2\text{CH}_3)$, NPh , $\text{N}(\text{C}_6\text{F}_5)$; and
- (4) changing the E group atom.

The variation described as point (4) has already been demonstrated in Chapter 4 with successive substitution of the chelating atom E ($\text{E} = \text{O}, \text{N}, \text{S}$). Other atoms could also be considered for substitution at E. For example, the compounds 2-selenopyridine⁵ (2), 2-pyridyldimethylsilane⁶ (3), and 2-pyridylmethyllithium⁷ (4) are known and could generate additional novel hexacoordinate phosphorus compounds from analogous reactions to those demonstrated in Chapter 4.

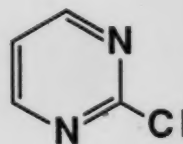


The approach given as point (3), modification of the E group in the 2 position, has also been demonstrated in Chapter 4 by the preparation of the λ^6 -phosphorane derivatives containing NMe and NPy amino groups. Substitution at this amino group (e.g. NEt, NBu^t, NPh, NC₆F₅) would lead to other derivatives with modified steric bulk and electronic arrangement at this nitrogen.

Altering the atoms within the pyridine ring itself is another possibility. Using other similar heterocyclic ring systems such as pyrazines and pyrimidines, which contain similar six-membered rings, one could generate an array of compounds analogous to those in Chapter 4. Both 2-chloropyrazine (5) and 2-chloropyrimidine (6) are commercially available, making the preparation of these chelates straightforward.



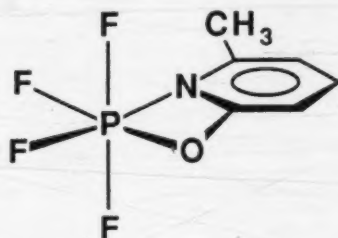
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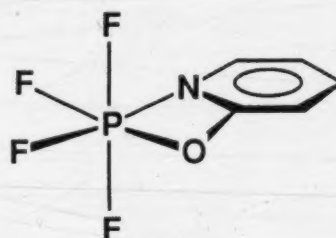
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Finally, there are numerous substitutions that can be made on the pyridine ring itself that would modify its chelating properties towards the acidic hexacoordinate phosphorus center. Known pyridine chemistry shows that substitutions at the 2 and 6 positions on the ring have the most effect on the nature of the ring nitrogen. For example, the pK_a of pyridine [5.20] and the chlorine substituted pyridines, such as 2-chloropyridine [0.72], 3-chloropyridine [2.84], 4-chloropyridine [3.84], 2,3-dichloropyridine [-0.85], 2,6-dichloropyridine [-2.86], and pentachloropyridine [-6.02], have been reported.⁸ Carefully positioned electron withdrawing (Cl, NO₂) and electron donating (Me, NMe₂) groups on the pyridine ring would generate an array of modified chelate ligands which would be structurally similar yet chemically different. This would allow the exploration of details of the interaction between the base and the phosphorus acid center. For example, would substitution of an electron-donating methyl group at the 6 position on the

2-hydroxypyridine ring generate a neutral hexacoordinate phosphorus compound (7) with slower fluorine exchange than compound 8 from Chapter 4 ?



7



8

These pyridine-based ligands can be chemically tailored in several ways to systematically study trends that affect the formation and nature of a neutral hexacoordinate phosphorus compound. Of the several routes open to future work, the use of modified pyridinol ligands has the highest potential for obtaining a greater insight into λ^6 -phosphorus chemistry.

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